A BRIEF INTRODUCTION TO POLYMERIC MATERIALS

by:

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1.0 Polymeric Materials.

A structural engineer who wishes to use adhesives must understand at least the rudiments of polymer chemistry, in much the same way that a structural engineer working with metal alloys must understand at least the rudiments of metallurgy. A brief introduction to polymer material science is given in the following subsections. The underlying objective of this discussion is to simply define some of the terms commonly used to classify or otherwise describe polymers. Since this introduction is necessarily brief, the reader desiring a more detailed discussion is referred to any of the many excellent introductory texts devoted to organic chemistry and/or polymeric materials, such as references 1 through 3. Although very "dated", you may also find the brief tutorial article by Richardson and Kierstead (Ref 4) helpful.

1.1 Atomic Structure: All matter is composed of *atoms*. An atom consists of a small and very dense core called the *nucleus*, which is "orbited" by smaller particles called *electrons*. The nucleus is made up of both *protons* and *neutrons*. The mass of protons and neutrons is about the same (1.6726×10^{-24} g and 1.6750×10^{-24} g, respectively), whereas the mass of electrons is four orders of magnitude lower (approximately 9.11×10^{-28} g). The proton is positively charged, the electron is negatively charged, and the neutron is electrically neutral. The *magnitude* of the electrical charge associated with protons and electrons is identical (approximately 1.602×10^{-19} Coulombs). The electrical charge of these *subatomic particles* is usually described in relative terms. That is, instead of specifying the charge in "Coulombs," the proton is said to have a charge of "+1", while the electron has a charge of "-1."

The *atomic number* of an atom equals the number of protons present within the nucleus, and is commonly designated by the symbol "Z." The number of neutrons within the nucleus is called the *neutron number* and is designated by the symbol "N." The *mass number* of an atom is designated "A," and equals the sum of the atomic number and neutron number: A = Z + N.

The "identity" of an atom is established by the atomic number, i.e., by the number of protons within the nucleus. For example, all oxygen atoms have an atomic number of 8, meaning that all oxygen atoms contain 8 protons within its' nucleus. However, the number of neutrons within the nucleus can vary for atoms of the same element. Therefore, atoms of the same element may have a range of mass numbers. For example, oxygen atoms may contain 8, 9, or 10 neutrons, so the mass number of oxygen may be 16, 17, or 18. Atoms that have the same atomic number but differing mass numbers are called *isotopes* of the element.

The *atomic mass number* is a common method of comparing the relative masses of different elemental atoms. By international agreement, the carbon-12 atom (i.e., an isotope of carbon containing 6 protons and 6 neutrons) is assigned an atomic mass number of *precisely* 12, and 1 atomic mass unit, *u*, is defined as *precisely* 1/12 of the mass of one carbon-12 atom. Numerically, $u = 1.6606 \times 10^{-24}$ g. Hence, the mass of a single proton, neutron, and electron equal 1.0073*u*, 1.0087*u*, and 0.000549*u*, respectively.

Atoms are electrically neutral, by definition. Since protons and electrons possess a relative charge of +1 and -1, respectively, it is therefore clear that atoms must contain an equal number of protons and electrons. As already mentioned, the electrons can be roughly visualized as "orbiting" the nucleus. This occurs because the negatively-charged electrons are attracted to the positively-charged nucleus. However, modern quantum theory has revealed that the electron(s) moving about the nucleus can do so only in discrete, well-defined paths or "shells." These shells correspond to different energy levels. Electron(s) within the innermost shells are very highly attracted to the nucleus, and are said to be tightly "bonded" to the nucleus. The bond between these innermost electrons and the nucleus is typically so strong that a massive amount of energy is required to "break" the bond. On the other hand, electron(s) in the outermost shell are less tightly bonded to the nucleus. In general, much less energy is required to "break" the bond between these outer electrons and the nucleus and, depending on the atom, the bond between an outer electron and the nucleus may be broken or formed relatively easily. Almost all chemical reactions involve the electrons within the outermost shells, and the electrons within these outermost shells are called *valence electrons*.

Since an atom may "lose" or "gain" valence electron(s), the atom may develop a net electrical charge. An atom that has lost or gained an electron is called an *ion*. If the atom loses an electron it becomes positively charged and is called a *cation*. Conversely, if the atom gains an electron it becomes negatively charged and is called an *anion*.

A periodic table of the elements is shown in Figure 1[1]. A total of 109 elements have been identified. The symbol used to designate each element as well as it's atomic number and atomic mass number are shown. One additional item of interest shown in Figure 1 is the concept of a *group* of elements, represented by several of the vertical columns within the periodic table. *Group numbers* are indicated in Figure 1 by Roman numerals ranging from I to VII . All of the elements within a group have similar properties because the electron configurations in their outermost electron shell are similar. That is, the group number of an element equals the total number valence electrons within the outermost shells of the atom.

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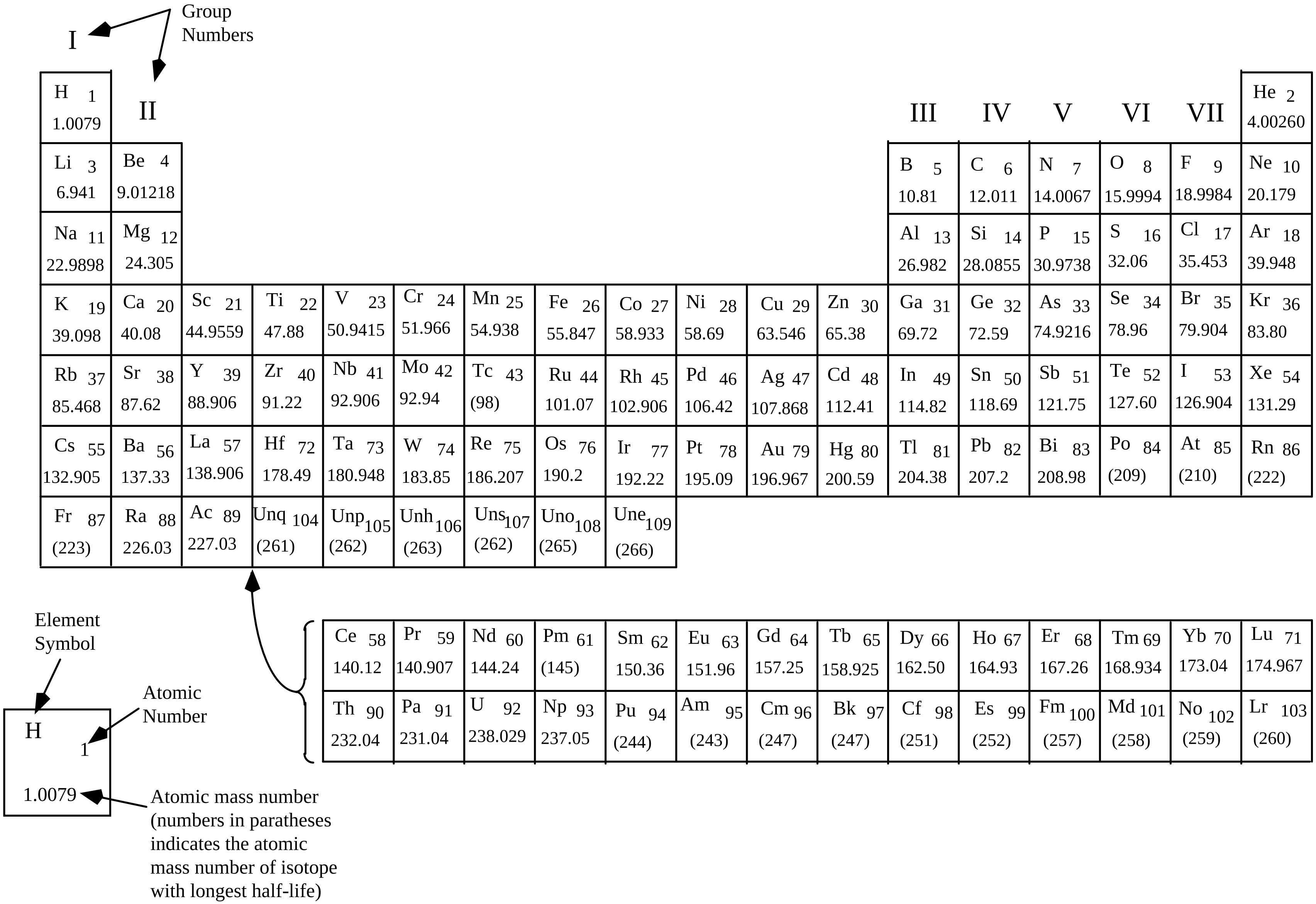
[1] This figure is based on a similar table shown in Ref [1], and does not contain all of the information that ordinarily appears in a periodic table of the elements.



I	II											III	IV	V	VI	VII	
H 1 1.0079																	He 2 4.00260
Li 3 6.941	Be 4 9.01218											B 5 10.81	C 6 12.011	N 7 14.0067	O 8 15.9994	F 9 18.9984	Ne 10 20.179
Na 11 22.9898	Mg 12 24.305											Al 13 26.982	Si 14 28.0855	P 15 30.9738	S 16 32.06	Cl 17 35.453	Ar 18 39.948
K 19 39.098	Ca 20 40.08	Sc 21 44.9559	Ti 22 47.88	V 23 50.9415	Cr 24 51.966	Mn 25 54.938	Fe 26 55.847	Co 27 58.933	Ni 28 58.69	Cu 29 63.546	Zn 30 65.38	Ga 31 69.72	Ge 32 72.59	As 33 74.9216	Se 34 78.96	Br 35 79.904	Kr 36 83.80
Rb 37 85.468	Sr 38 87.62	Y 39 88.906	Zr 40 91.22	Nb 41 92.906	Mo 42 92.94	Tc 43 (98)	Ru 44 101.07	Rh 45 102.906	Pd 46 106.42	Ag 47 107.868	Cd 48 112.41	In 49 114.82	Sn 50 118.69	Sb 51 121.75	Te 52 127.60	I 53 126.904	Xe 54 131.29
Cs 55 132.905	Ba 56 137.33	La 57 138.906	Hf 72 178.49	Ta 73 180.948	W 74 183.85	Re 75 186.207	Os 76 190.2	Ir 77 192.22	Pt 78 195.09	Au 79 196.967	Hg 80 200.59	Tl 81 204.38	Pb 82 207.2	Bi 83 208.98	Po 84 (209)	At 85 (210)	Rn 86 (222)
Fr 87 (223)	Ra 88 226.03	Ac 89 227.03	Unq 104 (261)	Unp 105 (262)	Unh 106 (263)	Uns 107 (262)	Uno 108 (265)	Une 109 (266)									

Ce 58 140.12	Pr 59 140.907	Nd 60 144.24	Pm 61 (145)	Sm 62 150.36	Eu 63 151.96	Gd 64 157.25	Tb 65 158.925	Dy 66 162.50	Ho 67 164.93	Er 68 167.26	Tm 69 168.934	Yb 70 173.04	Lu 71 174.967
Th 90 232.04	Pa 91 231.04	U 92 238.029	Np 93 237.05	Pu 94 (244)	Am 95 (243)	Cm 96 (247)	Bk 97 (247)	Cf 98 (251)	Es 99 (252)	Fm 100 (257)	Md 101 (258)	No 102 (259)	Lr 103 (260)

Figure 1(a): Periodic Table of the Elements (following [1])

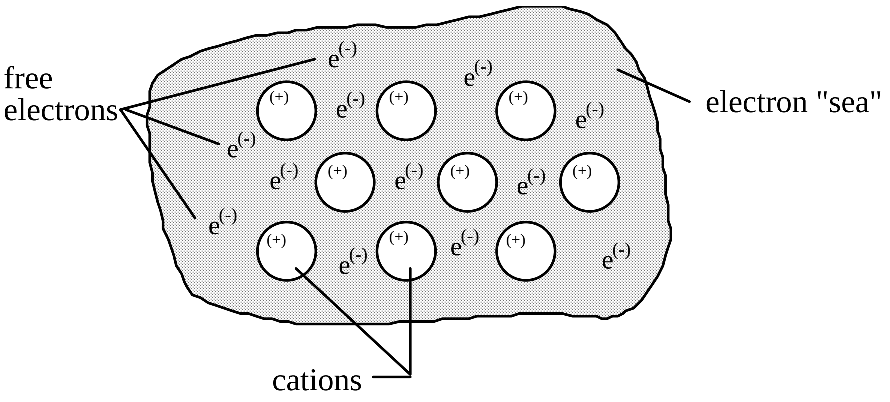
Figure 1(b): Alphabetical listing of the elements [1]

Element	Symbol	Atomic Number		Element	Symbol	Atomic Number
Actinium	Ac	89		Neon	Ne	10
Aluminum	Al	13		Neptunium	Np	93
Americium	Am	95		Nickle	Ni	28
Antimony	Sb	51		Niobium	Nb	41
Argon	Ar	18		Nitrogen	Ni	7
Arsenic	As	33		Nobelium	No	102
Astatine	At	85		Osmium	Os	76
Barium	Ba	56		Oxygen	O	8
Berkelium	Bk	97		Palladium	Pd	46
Beryllium	Be	4		Phosphorous	P	15
Bismuth	Bi	83		Platinum	Pt	78
Boron	B	5		Plutonium	Pu	94
Bromine	Br	35		Polonium	Po	84
Cadmium	Cd	48		Potassium	K	19
Calcium	Ca	20		Praseodymium	Pr	59
Californium	Cf	98		Promethium	Pm	61
Carbon	C	6		Protactinium	Pa	91
Cerium	Ce	58		Radium	Ra	88
Cesium	Cs	55		Radon	Rn	86
Chlorine	Cl	17		Rhenium	Re	75
Chromium	Cr	24		Rhodium	Rh	45
Cobalt	Co	27		Rubidium	Ru	37
Copper	Cu	29		Ruthenium	Ru	44
Curium	Cm	96		Samarium	Sm	62
Dysprosium	Dy	66		Scandium	Sc	21
Einsteinium	Es	99		Selenium	Se	34
Erbium	Er	68		Silicon	Si	14
Europium	Eu	63		Silver	Ag	47
Fermium	Fm	100		Sodium	Na	11
Fluorine	F	9		Strontium	Sr	38
Francium	Fr	87		Sulfur	S	16
Gadolinium	Gd	64		Tantalum	Ta	73
Gallium	Ga	31		Technetium	Tc	43
Germanium	Ge	32		Tellurium	Te	52
Gold	Au	79		Terbium	Tb	65
Hafnium	Hf	72		Thallium	Tl	81
Helium	He	2		Thorium	Th	90
Holmium	Ho	67		Thulium	Tm	69
Hydrogen	H	1		Tin	Sn	50
Indium	In	49		Titanium	Ti	22
Iodine	I	53		Tungsten	W	74
Iridium	Ir	77		Unnilennium	Une	109
Iron	Fe	26		Unnilhexium	Unh	106
Krypton	Kr	36		Unniloctium	Uno	108
Lanthanum	La	57		Unnilpentium	Unp	105
Lawrencium	Lr	103		Unniquadium	Unq	104
Lead	Pb	82		Unnilseptium	Uns	107
Lithium	Li	3		Uranium	U	92
Lutetium	Lu	71		Vanadium	V	23
Magnesium	Mg	12		Xenon	Xe	54
Manganese	Mn	25		Ytterbium	Yb	70
Mendelvium	Md	101		Yttrium	Y	39
Mercury	Hg	80		Zinc	Zn	30
Molybdenum	Mo	42		Zirconium	Zr	40
Neodymium	Nd	60				

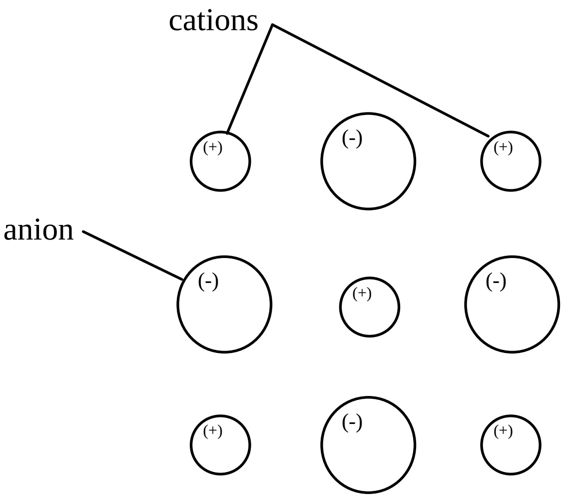
1.2 Chemical Bonds: The term "chemical bond" refers to the attractive forces that cause two (or more) atoms to bond together so as to form a recognizable chemical entity. The "new" chemical entity normally exhibits properties that differ from the original constituent atom(s). There are three fundamental types of chemical bonds: *metallic bonds*, *ionic bonds*, and *covalent bonds*. Note that these forces occur at the atomic level. A second category of forces can be defined at the molecular level. The magnitude of these *intermolecular forces* (or *"secondary forces"*) are much less than those associated with chemical bonding, as will be discussed in section 1.3.

1.2.1. Metallic Bonds. Metallic bonding is illustrated schematically in Figure 2(a). Metallic bonding generally occurs for elements that have only one or two valence electrons, since these elements can easily lose electrons to form positively charged cations. Each atom contributes an electron(s) to a "sea" of electrons surrounding the cations. That is, the electrons do not "belong" to any individual cation but rather are free to move within the atomic structure. Metallic bonding is most commonly encountered in the elemental metals or metallic alloys. The very high electrical and thermal conductivities exhibited these materials is a direct result of the mobile electron sea which exists at the atomic level. Note that independent molecules do not exist within substances formed by metallic bonding. Most polymers do not involve metallic bonds, and hence the polymer chemist is not often concerned with this form of chemical bonding.

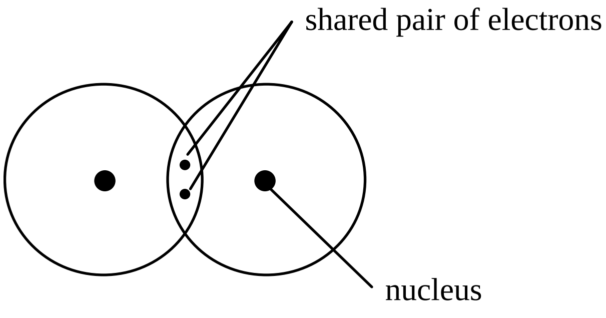
1.2.2. Ionic Bonds. The ionic bond is illustrated in Figure 2(b). Ionic bonding occurs as a result of the electrostatic attraction between positive cations and negative anions. *Ionic compounds* are substances formed by ionic bonding. As in the case of metallic bonding, independent molecules do not exist within ionic compounds. Ionic compounds do not contain mobile electrons, and consequently are poor conductors of electrical or thermal energy.



(a) Illustration of Metallic Bonding



(b) Illustration of Ionic Bonding



(c) Illustration of Covalent Bonding
Figure 2: Schematic Representation of the Three Fundamental Types of Chemical Bonds: Metallic, Ionic, and Covalent Bonding [1]

The *octet rule* can be used to predict which elements will form stable ionic compounds. According to this rule a stable ionic bond will form between two (or more) atoms if the atoms can lose or gain electrons such that the outermost shell of each atom involved contains eight electrons.

1.2.3. Covalent Bonds. The covalent bond is the most important type of chemical bonding in polymers, and occurs in virtually all polymeric materials. A covalent bond is formed when two atoms "share" a pair of electrons, as shown schematically in Figure 2(c). In contrast to metallic or ionic bonds, independent molecules are formed by covalent bonds.

Note that the number of electrons associated with an atom does not decrease when a covalent bond is formed; neither atom "loses" an electron. However, the pair of electrons that form the covalent bond are more likely to occupy the space between the two nuclei than would ordinarily be the case. The increased likelihood that the electrons occupy the region of space between the two nuclei is described by saying that the *electron density* of the space between the two nuclei is increased as a result of covalent bonding. The covalent bond results because of the electrostatic forces of attraction between the positively-charged nuclei and the negatively-charged region of high electron density. A *single covalent bond* is a bond that involves a single pair of electrons. In a *double or triple covalent bond* two atoms share two or three pairs of electrons, respectively.

The *octet rule* can be used to predict the number of covalent bonds a given element can form[2]. According to this rule two atoms will share electrons such that the outermost shell of both atoms contains eight electrons. Thus, the number of covalent bonds a given element can form can be determined by subtracting the group number from 8. For example, referring to the periodic table shown in Figure 1, it is seen that the element carbon (C) is listed in group IV, and can therefore form four (8-4 = 4) covalent bonds. Similarly, oxygen (O) is listed in group VI and can form two covalent bonds.

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[2] There are exceptions to the octet rule that are not described in this review. The interested reader is referred to Chapter 10 of Reference 1.

The preceding discussion has implied that the electrons within a covalent bond are shared "equally" by both atomic nuclei. This is only true when the two atomic nuclei that form the bond attract the electrons pair equally. Since the magnitude of attractive force is established by the number of protons in the nucleus, the electron pair is only shared equally if both atoms have the same number of protons, i.e., if both atoms are of the same element. Examples of this type of molecule are H_2, Cl_2, or N_2. In these cases the electron density is equal for both atoms within the molecule and the bond is called a *nonpolar covalent bond*.

In contrast, if a covalent bond is formed in which one atom exerts a stronger attractive force than the other, then the electron density around one atom is greater than the other and a *polar covalent bond* is developed. In effect, the atom with the greater electron density develops a partial negative charge (δ^-, say) while the atom with the lower electron density develops a partial positive charge (δ^+, say). This usually occurs when a covalent bond is formed between atoms of different elements (because the nucleus of the two elements possess a different number of protons), but can also occur between atoms of the same element if the atoms are a part of a larger molecule. The difference between a nonpolar covalent bond and a polar covalent bond is shown schematically in Figure 3.

A polar molecule exhibits non-uniform electron densities, and can be treated as a *dipole*. That is, although the molecule remains electrically neutral as a whole, one region of the molecule develops a negative charge while a second region develops a positive charge of equal magnitude. The two electrically-charged regions exist at a specific distance from each other, forming an electrical dipole. The negatively-charged region of a polar molecule is attracted to the positively-

(a) Nonpolar Covalent Bond

(b) Polar Covalent Bond

Figure 3: Difference Between a "Nonpolar" and "Polar" Covalent Bond

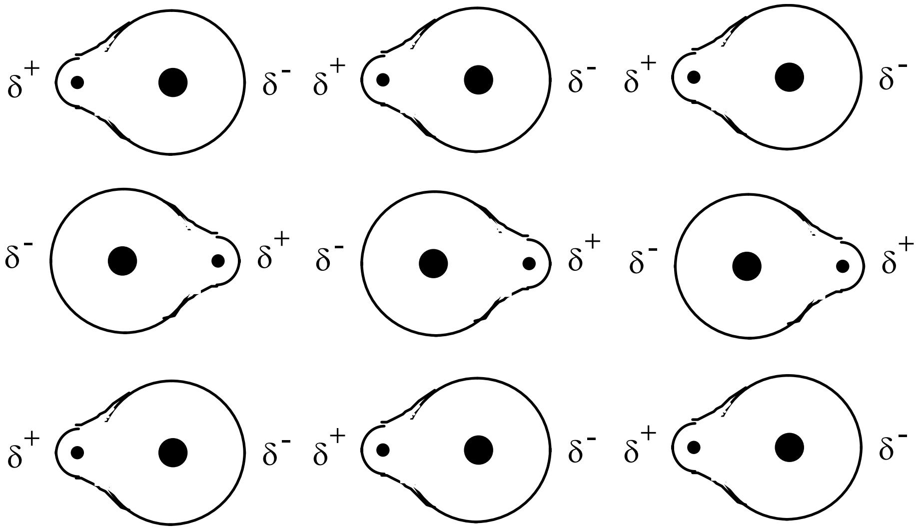

Figure 4: Schematic Representation of Dipole-Dipole Interactions in a Polar Covalent Compound [1]

charged regions of neighboring polar molecules, as shown schematically in Figure 4. Hence, dipole-dipole interactions between polar molecules leads to a type of "secondary" bonding between molecules, as more fully described in section 1.3.

Note that while the distinction between "metallic", "ionic", and "covalent" bonding is a convenient way of classifying chemical bonds, in reality chemical bonding is rarely "100%" metallic, ionic, or covalent. For example, the polar covalent bond illustrated in Figure 3(b) could be described as a "polar, partly ionic, covalent bond."

1.2.4 Covalent Bond Lengths and Strengths: Figure 2(c) illustrates that a covalent bond can only form if two atoms are sufficiently close to each other, such that the "electron cloud" surrounding each atom can overlap. The covalent bond is formed due to forces of attraction between the positively-charged nuclei and the negatively-charged region of high electron density. However, repulsive forces also exist between the two positively-charged nuclei as well as the two

Table 1: Bond Lengths and Bond Energies for Representative Covalent Bonds [1]

Atoms	Bond Length (nm)	Bond Energy (kcal/mole)	Bond Energy (kJ/mole)
H-H	0.074	104	435
H-Cl	0.127	103	431
Cl-Cl	0.198	58	243
H-C	0.109	99	414
C-C	0.154	79	331
C=C	0.134	141	590
C≡C	0.120	194	812
C-O	0.143	78	326
C=O	0.120	192	803
C≡O	0.113	257	1075
N-N	0.145	38	159
N=N	0.125	113	473
N≡N	0.110	226	946

negatively-charged electron clouds. Hence, for any covalent bond there is an "equilibrium spacing" between nuclei; that is, the distance between nuclei at which the forces of attraction are exactly balanced by the forces of repulsion. This equilibrium spacing between nuclei is called the covalent *bond length*. The energy needed to pull the two nuclei apart, thereby destroying the covalent bond, is called the *bond energy*. [3] Bond lengths and bond energies for covalent bonds often encountered in polymeric substances are listed in Table 1. Note that the bond lengths are exceedingly small; on the order of a tenth of a nanometer (1 nm = 10^{-9} m). Also note that bond energies are often reported in units of either kcal/mole or kJ/mole, where 1 calorie = 4.19 Joules.

1.3 Intermolecular Forces: The phrase "intermolecular forces" refers to forces of attraction (or repulsion) between molecules or sections of molecules, and are generally of much lower magnitude than interatomic forces associated with chemical bonding. Although names and classifications vary from author-to-author, four principal types of intermolecular forces are generally recognized: *dipole-dipole forces*, *dipole-induced dipole forces*, *London forces (also called dispersion or van der Waal forces)*, and *hydrogen bonding*. Intermolecular forces are often referred to as "secondary bonds."[4]

1.3.1: Dipole-dipole forces: The source of dipole-dipole forces has been described in section 1.2.3 - they arise because the positive end of a polar molecule is attracted to the negative end of a neighboring polar molecule. These forces are sometimes referred to as *permanent dipole-dipole forces*, because they arise from polar molecules that are "permanent" dipoles.

1.3.2: Dipole-induced dipole forces: A polar molecule (i.e., a permanent dipole) may cause a shift in the electron density of a neighboring nonpolar molecule. Thus, the initially nonpolar molecule becomes a *temporary or induced dipole*. Dipole-induced dipole forces (sometimes

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[3] Various authors also refer to the bond energy as the *"bond strength"* or the bond *"dissociation energy"*.
[4] Some authors do not include hydrogen bonds within the category of "secondary bonds."

referred to as *Keesom forces*) are the forces of attraction between the permanent and induced dipoles.

1.3.3: London (or dispersion) forces: London forces are also due to shifts in the electron density of a nonpolar molecule, which result in temporary dipoles. However, in contrast to Keesom forces, London forces are caused by interactions between *two* temporary dipoles. One end (or region) of a molecule momentarily develops a slight positive charge, say, which consequently means that the other end (or a second region) momentarily develops a slight negative charge. The positive end/region of the molecule will induce a slight negative charge in an adjacent region of a neighboring molecule, causing an asymmetric electron density in this neighboring molecule. London forces are the forces of attraction between fluctuating induced dipoles. London forces are extremely significant in that they are present in all covalently bonded substances, whether polar or non-polar.

1.3.4: Hydrogen bonding: Although hydrogen bonding is customarily listed as a separate type of intermolecular force, in reality hydrogen bonding is simply an unusually strong dipole-dipole force. It occurs when a hydrogen atom is covalently bonded to a relatively small but strongly electronegative atom. In particular, strong hydrogen bond forces result when a hydrogen atom is covalently bonded to a fluorine, nitrogen, or oxygen atom. Since the hydrogen atom carries only a single electron and proton, once the covalent bond is formed with these larger atoms the much smaller hydrogen atom has very little electron density surrounding it, and a strongly polar molecule results. The hydrogen atom develops an unusually large (partial) positive charge. Therefore, in addition to being covalently bonded to an electronegative atom, the hydrogen atom is strongly attracted to a second surrounding electronegative atom.

1.3.5 The strength of intermolecular forces: Inter-molecular forces are present in all molecular substances, and determine whether the substance is a gas, a liquid, or a solid at a given temperature. Unlike covalent bonds, is not possible to define the "bond length" of a secondary bond, since the nature and strength of the bond depends on the molecules involved. However, a few general statements regarding the nature of all intermolecular forces can be made. First, significant intermolecular forces exist only over very short distances. Furthermore, the strength of intermolecular forces decreases rapidly with intermolecular spacing, and the rate of decrease is typically inversely proportional to the distance raised to the 7th power (d^{-7}, where d = average intermolecular spacing). Therefore, *any* mechanism that leads to an increase in average molecular spacing can be expected to cause pronounced decrease in intermolecular forces, which often become apparent through dramatic changes in the macroscopic properties of the substance. A common example is the introduction of heat: if the temperature of an initially solid molecular substance is raised, the increase in thermal energy causes an increase in the average molecular spacing. If enough thermal energy is added then intermolecular forces are decreased to the point that the substance becomes liquidous and "melts." If sufficient additional heat is added the intermolecular forces are further decreased until the liquid becomes gaseous and "evaporates."

As in intermolecular bond lengths, the strength of intermolecular forces cannot be precisely defined due to the infinite possible combinations of molecules. However, the range in various intermolecular forces can be estimated and are listed in Table 2. Note that the hydrogen bond results in the strongest intermolecular force. Comparing bond energies listed in Tables 1 and 2, it is immediately apparent that intermolecular forces are typically at least one order of magnitude lower than interatomic forces.

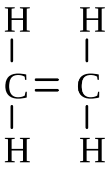
Table 2: Representative Bond Energies of Intermolecular Forces [5]

Type	Bond Energy (kcal/mole)	Bond Energy (kJ/mole)
Hydrogen Bonds	2 - 24	10-100
Dipole-dipole	1 - 5	4 - 20
Dipole-induced dipole (Keesom)	< 0.5	< 2
London (dispersion)	0.02 - 10	0.08 - 40

1.4 Fundamental Aspects of Polymer Molecules: The term "polymer" comes from the Greek words *poly* (meaning "many") and *mers* (meaning "units"). At the molecular level polymers consist of extremely long, chain-like molecules. Polymer molecules are typically made up of thousands of repeating chemical units, and have molecular weights ranging from about 10^3 to 10^7.

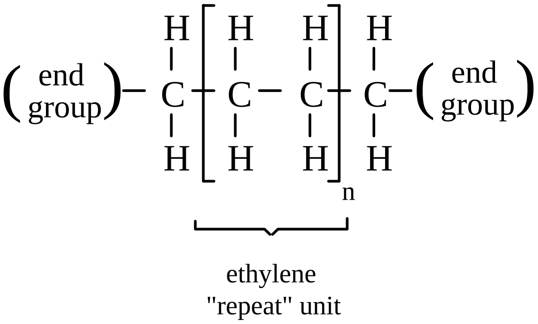
As an illustrative example, consider the single chemical mer shown in Figure 5. This mer is called *ethylene* (or *ethene*), and consists of two carbon atoms and four hydrogen atoms. The two lines between the carbon (C) atoms indicate a double covalent bond whereas the single line between the hydrogen (H) and carbon atoms represents a single covalent bond. The chemical composition of the ethylene mer is written C_2H_4 or $CH_2=CH_2$. Under the proper conditions one of the double covalent bonds between the two carbon atoms can be broken, which allows each of the two carbon atoms to form a new covalent bond with a carbon atom in a neighboring mer. In this way three ethylene mers form a "new" molecule, whose atomic weight is three times as great as the initial mer. If "n" ethylene mers join together, the chemical composition of the resulting molecule can be represented $C_{2n}H_{4n}$, where n is any positive integer. In this way a "chain" of ethylene mers join together to form the well-known polymer *polyethylene*, as shown in Figure 6. A typical polyethylene molecule may contain 50,000 carbon atoms or more. The process of causing a monomer to chemically react and form long molecules in this fashion is called *polymerization*, and the number of repeating units which make up the molecule is called the *degree of polymerization*.

The single ethylene unit is an example of a *monomer*. At room temperatures a bulk sample of the ethylene monomer is a low-viscosity fluid. If two ethylene monomers bond together the resulting chemical entity has two repeating units and is called a "*dimer*." Similarly, the chemical entity formed by three repeating units is called a "*trimer*." The molecular weight of a dimer is twice that of the monomer, the molecular weight of a trimer is three times that of the monomer, etc. Prior



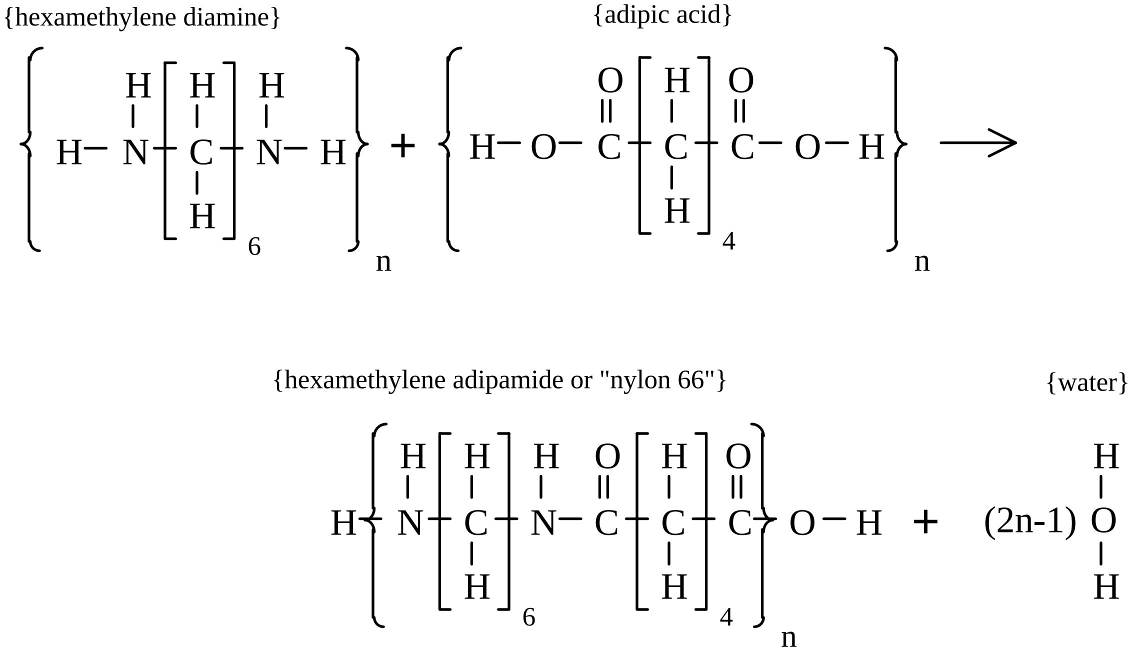
$$\underset{H}{\overset{H}{C}}=\underset{H}{\overset{H}{C}}$$

Figure 5: The monomer "ethylene"



$$(\text{end group})-\underset{H}{\overset{H}{C}}-\underbrace{\left[\underset{H}{\overset{H}{C}}-\underset{H}{\overset{H}{C}}\right]_n}_{\text{ethylene "repeat" unit}}-\underset{H}{\overset{H}{C}}-(\text{end group})$$

Figure 6: The polymer "polyethylene"



$$\left\{H-\overset{H}{N}-\left[\underset{H}{\overset{H}{C}}\right]_6-\overset{H}{N}-H\right\}_n+\left\{H-O-\overset{O}{\overset{\|}{C}}-\left[\underset{H}{\overset{H}{C}}\right]_4-\overset{O}{\overset{\|}{C}}-O-H\right\}_n\longrightarrow$$

$$H\left\{\overset{H}{N}-\left[\underset{H}{\overset{H}{C}}\right]_6-\overset{H}{N}-\overset{O}{\overset{\|}{C}}-\left[\underset{H}{\overset{H}{C}}\right]_4-\overset{O}{\overset{\|}{C}}\right\}_n O-H+(2n-1)\,\underset{H}{\overset{H}{O}}$$

Figure 7: The Polymer "Nylon 66"

to polymerization most polymers exist as low-viscosity fluids known as *oligomers* (from the Greek term *oligo* meaning "a few"). An oligomer consists of chemical entities with a range of molecular weights, typically containing perhaps 1-10 mers.

The viscosity of an initially fluid oligomer rapidly increases as polymerization occurs and molecular weight increases. Eventually the polymer becomes more a "solid" than a "fluid". Nevertheless, the solid polymer retains some "fluid-like" features, e.g., all polymers are viscoelastic to some extent.

It should be clear from the above discussion that a polymer does not have a specific molecular weight. Rather, all polymer samples exhibit some range in molecular weight. The *average molecular weight* is increased as the polymerization process is initiated and the degree of polymerization is increased. As mentioned above a low-density polyethylene molecule contains 50,000 carbon atoms (or more), which corresponds to an average molecular weight in the vicinity of 10^4 (or more).

Although a polymeric molecule is extremely large, it is nevertheless finite, and the molecular chain must eventually terminate. The chemical entities that bond to the ends of a polymer molecule are called *end groups*, and are usually different than the repeat unit. For a commercially-available polymer such as polyethylene the chemical nature of the end groups is not specified, and depends on the polymerization conditions and catalyst used to initiate the polymerization process. Hence, a bulk sample of "polyethylene" produced by manufacturer "A" will likely have different end groups, and hence slightly different elemental chemical constituents, than a bulk sample of "polyethylene" produced by manufacturer "B."

The *functionality* (or *valency*) of a mer equals the number of covalent bonds the mer can form with other chemical groups. Ethylene can form two bonds, and hence is called a *difunctional* mer.

A *monofunctional* mer can form only one covalent bond, and therefore cannot exist as the repeat unit in a polymer, although a monofunctional mer can exist within a polymer as an end group. *Trifunctional* or *tetrafunctional* mers can form three or four covalent bonds, respectively.

Although in the case of polyethylene the repeat unit is equivalent to the original ethylene monomer, this is not always the case. In fact, in many instances the repeat unit is derived from two (or more) monomers. A typical example is Nylon 66. The polymerization process for this polymer is shown schematically in Figure 7. Two monomers are used to produce Nylon 66: hexamethylene diamine (chemical composition: $C_6H_{16}N_2$) and adipic acid (chemical composition: $COOH(CH_2)_4COOH$). Note that the repeat unit of Nylon 66 (hexamethylene adipamide) is not equivalent to either of the two original monomers.

A low-molecular weight byproduct (i.e., water) is produced during the polymerization of Nylon 66. This is a characteristic of *condensation polymers*. That is, if both a high-molecular weight polymer as well as a low-molecular weight byproduct is formed during the polymerization process, the polymer is classified as a condensation polymer. Conversely, *addition polymers* are those for which no byproduct is formed during the polymerization process, which implies that all atoms present in the original monomer(s) occur somewhere within the repeat unit. Generally speaking, condensation polymers shrink to a greater extent during the polymerization process than do addition polymers. Residual stresses caused by shrinkage during polymerization (sometimes referred to as "cure stresses") are often a concern in adhesive bonding, and hence difficulties with residual stresses can be minimized if an addition polymer is used in these structural applications.

1.3 Covalent Bond Angles: As previously discussed an individual molecule consists of elemental atoms bonded together via covalent bonds. A particularly simple molecule is the gas methane, CH_4. In this case the carbon atom is bonded to four hydrogen atoms via four single covalent bonds. A 3-D sketch of a single methane molecule is shown in Figure 8. As indicated, if the single molecule were completely isolated from all other “external effects” (where an “external effect” might be another methane molecule, for example), then the molecule will take on the shape of a four-sided regular tetrahedron. A *covalent bond angle* is defined as the angle between three neighboring atoms in a molecule. For example, the bond angle formed by the H-C-H atoms in a methane molecule (isolated from all external effects) is 109° 28’, as shown in Figure 8. This bond angle can be considered to the “equilibrium” value. That is, if external forces *are* present (such as the close proximity of another methane molecule, for example), then the molecule may be distorted, i.e., the covalent bond angle may deviate from 109° 28’. Note that since some work must be done on the molecule to cause this distortion, the “internal energy” of the molecule has been increased due to this distortion.

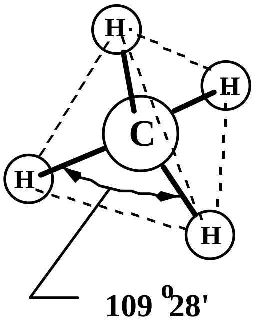
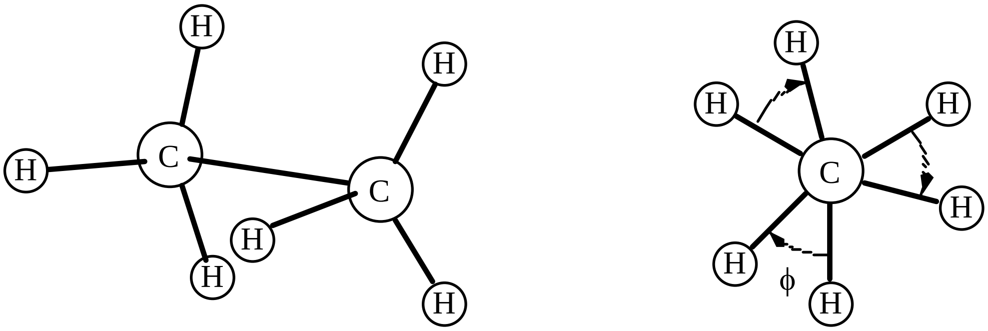


Figure 8: 3-D sketch of methane molecule, isolated from all external effects

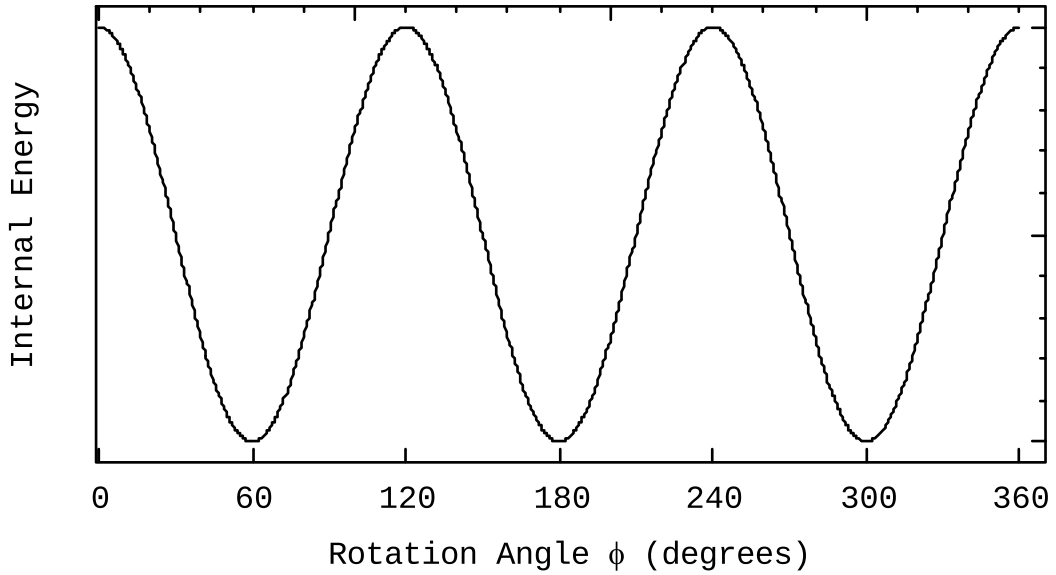
Of course, multiple covalent bond angles can be defined for more complex molecules, since complex molecules may involve many different elemental atoms and/or greater numbers of atoms than the simple methane molecule. Nevertheless, it is possible to calculate “equilibrium” values for all bond angles involved in a molecule, and if the bond angles deviate from their equilibrium values the “internal energy” of the molecule has been increased.

A second form of molecular “distortion” occurs through rotation about covalent bonds. This is illustrated in Figure 9 for the ethane molecule (C_2H_6). A 3-D sketch of the molecule is shown in



(a) 3-D sketch

(b) View along the C-C
covalent bond, showing rotation ϕ



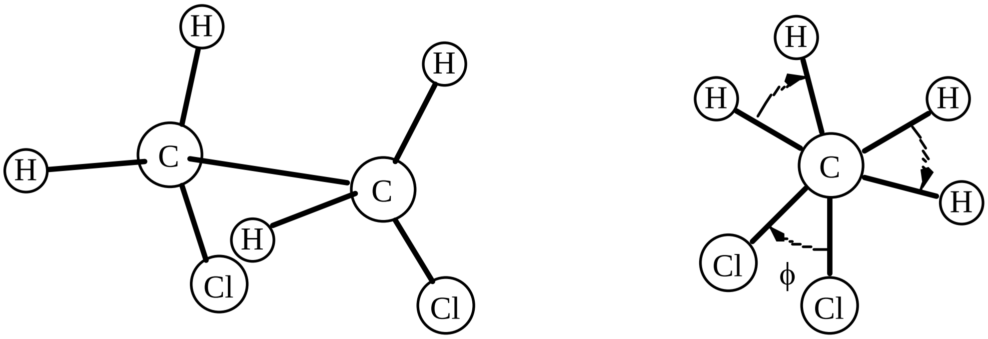
(c) Schematic plot of internal energy as a function of rotation about the covalent bond between the two carbon atoms.

Figure 9: Change in internal energy for an ethane molecule associated with rotation about a single covalent bond

Figure 9(a). In Figure 9(b) the molecule is viewed along the axis defined by the covalent bond between the two carbon atoms, and angle ϕ is used to denote rotation about this bond.

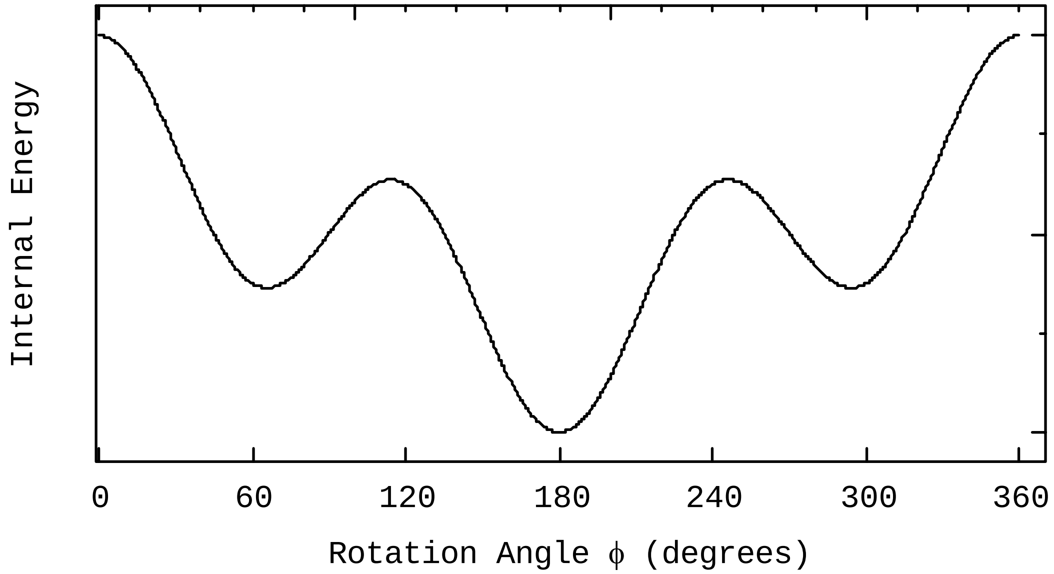
Figure 9(c) indicates schematically the variation in internal energy as a function of angle ϕ. Due to the symmetry associated with the two CH_3 groups, three equilibrium positions are possible for one cycle of rotation: $\phi = 60°$, 180°, and 300°. A second example is shown in Figure 10 for the ethylene chloride molecule, $C_2Cl_2H_4$. In this case the $CClH_2$ groups are not symmetric, and only one global equilibrium position exists for one cycle of rotation (at $\phi = 180°$), although two metastable positions exist (at $\phi = 60°$ and 300°).

Rotation about single covalent bonds can occur with a relatively modest increase in internal energy. Rotation about double or triple covalent bonds requires a much greater increase in energy. Hence, double and triple covalent bonds are said to be much “stiffer” than single covalent bonds. Notice from Figure 7 that a complex molecule (such as that of Nylon 66) usually involves single, double, and (occasionally) triple covalent bonds. Hence, some segments along a polymeric molecule are inherently much “stiffer” than other segments. In liquid form polymeric molecules rotate continously about single covalent bond. In contrast, in solid form polymeric molecules are “frozen” in a particular shape, and can rotate about covalent bonds only slowly, if at all.



(a) 3-D sketch

(b) View along the C-C covalent bond, showing rotation ϕ



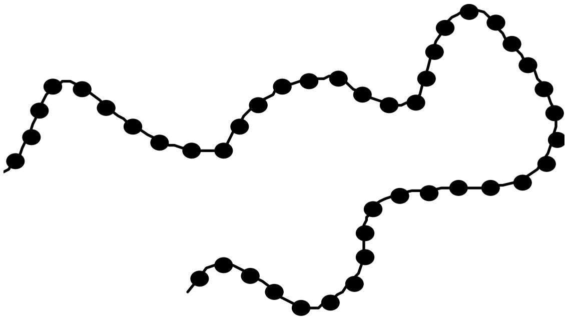
(c) Schematic plot of internal energy as a function of rotation about the covalent bond between the two carbon atoms.

Figure 10: Change in internal energy for an ethylene chloride molecule associated with rotation about a single covalent bond

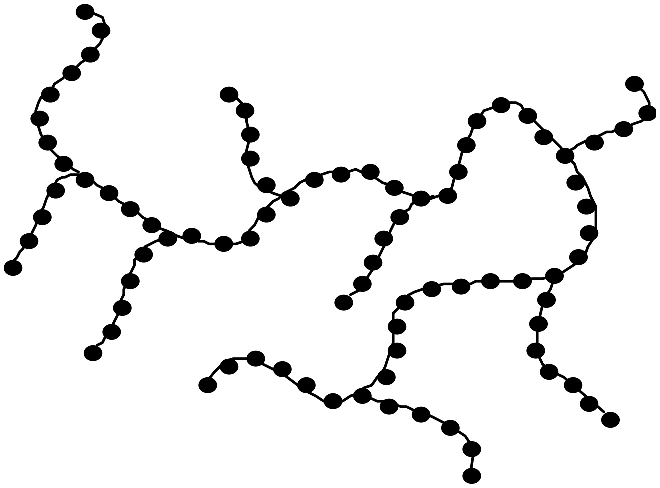
1.4 Overall Polymer Molecular Structure: The molecular structure of a fully polymerized polymer can be classified according to one of three major types: *linear, branched*, or *crosslinked* polymers. The three types of molecular structure are shown schematically in Figure 11.

Linear polymers can be visualized as beads on a string, where each bead represents a repeat unit. It should be emphasized that the length of these "strings" is enormous; if a typical linear molecule were scaled up to be 10 mm (0.4 in) in diameter, it would be roughly 4 km (2.5 mi) long. A linear polymer is formed by difunctional monomer(s). In a bulk sample these long *macromolecules* become entangled and twisted together, much like a bowl of cooked spaghetti. Obviously, as the molecular weight (i.e., the length) of the polymer molecule is increased, the number of entanglements is increased. Also, as the molecular weight is increased the secondary bonding forces between molecules is increased. Hence, at the macroscopic scale the elastic stiffness (i.e. Young's modulus) exhibited by a bulk polymer is directly related to the molecular weight.

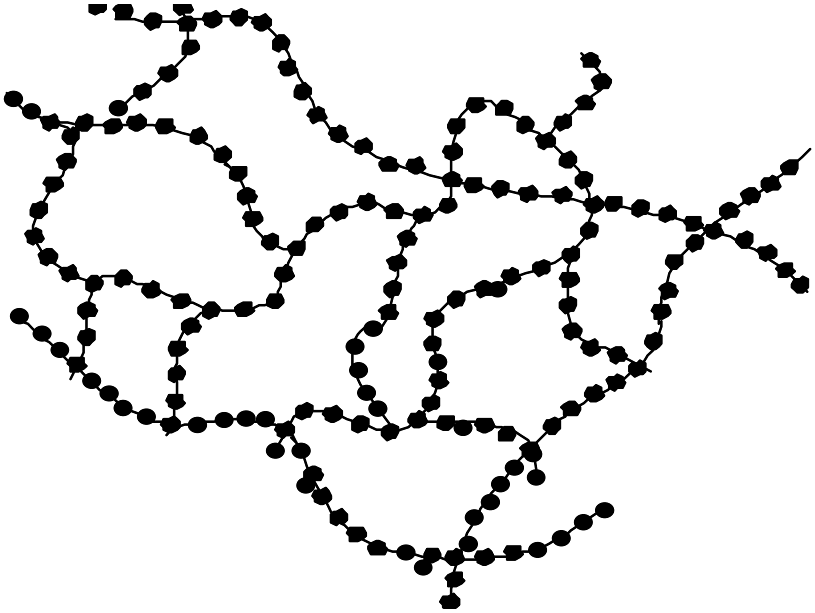
If all of the repeat units within a linear polymer are identical, the polymer is called a *homopolymer*. Polyethylene is a good example of a linear homopolymer. However, it is possible to produce linear polymers that consist of two separate and distinct repeat units. Such materials are called *copolymers*. In *linear random copolymers* the two distinct repeat units appear randomly along the backbone of the molecule. In contrast, for *linear block copolymers,* the two distinct repeat units form long continuous segments within the polymer chain. An example of a common copolymer is acrylonitrile-butadiene-styrene, commonly known as "ABS."



(a) Linear



(b) Branched



(c) Crosslinked

Figure 11: Types of Polymer Molecular Structure

The second major type of polymeric molecular structure is the *branched polymer* (see Figure 11). In branched polymers relatively short side chains are covalently bonded to the primary backbone of the macromolecule. The monomers that form branched polymers must be at least trifunctional. As before, the stiffness of a bulk sample of a branched polymer is directly related to both the molecular weight and the number of entanglements. Since the branches greatly increase the number of possible entanglements, the macroscopic stiffness of a branched polymer will, in general, be greater than the macroscopic stiffness of a linear polymer of identical molecular weight. In most branched polymers the branches consist of the same chemical repeat unit as the backbone of the molecular chain. However, for some polymers a branch with repeat unit B can be "grafted" onto a linear molecule with repeat unit A. Such materials are called *graft copolymers*.

Finally, the third major type of molecular structure is the *crosslinked or network polymer* (see Figure 11). The monomers that form crosslinked polymers must be at least trifunctional. During polymerization of such polymers a *crosslink* (i.e., a covalent bond) is formed between individual molecular chains. Hence, once polymerization is complete a vast molecular network is formed.

Returning to the analogy of a bowl of cooked spaghetti, one can imagine that a single spaghetti noodle could be extracted without damage if the noodle were pulled slowly and carefully, allowing the noodle to "slide" past its' neighbors, until the noodle was completely free from the "bulk" spaghetti. In much the same way, an individual molecule could be extracted (at least conceptually) from a bulk sample of a linear or branched polymer, since these polymers exist in the form of individual molecules. This is not the case for a fully polymerized crosslinked polymer, however. Since the "individual" molecular chains within a crosslinked polymer are themselves linked together by covalent bonds, the entire molecular network can be considered a single molecule. Common examples of a crosslinked polymer are crosslinked (or *vulcanized*) natural rubber, silicon rubber or epoxy.

1.6 Thermoplastic vs Thermoset Polymers: Suppose that a bulk sample of a *linear* or *branched* polymer exists as a solid material at room temperature, and is subsequently heated. Due to the increase in thermal energy, the average distance between individual molecular chains is increased as temperature is increased. This results in an increase in molecular mobility and a decrease in secondary bonding forces and macroscopic stiffness. That is, as the molecules move apart both the intermolecular forces of attraction as well as the degree of entanglement is decreased, resulting in a decrease in stiffness at the macroscopic level. Eventually a temperature is reached at which the polymeric molecules can slide freely past each other, and the bulk polymer "melts"- that is, the polymer can no longer support a shear force. Typically, melting does not occur at a single temperature, but rather over a temperature range of about 15-20°C. A polymer that can be melted (i.e., a linear or branched polymer) is called a *thermoplastic polymer*.

In contrast, a crosslinked polymer cannot be melted. Although the average distance between individual segments of the molecular network are in fact increased as temperature is increased, the crosslinks do not allow unrestricted relative motion between chain segments, and eventually limit molecular motion. Therefore, a crosslinked polymer cannot be melted and can support shear forces even at high temperatures. Of course, if the temperature is raised high enough the covalent bonds that form the crosslinks as well as the "backbone" of the molecular chains are broken, chemical degradation occurs, and the polymer is destroyed. A polymer that cannot be melted (i.e., a crosslinked polymer) is called a *thermoset polymer*.

Three more-or-less distinct conditions are recognized during the process of polymerizing a thermoset polymer. The original resin or oligomer is typically a low-viscosity, low-molecular weight fluid, containing molecules with perhaps 2-10 repeat units. The thermoset resin is said to be *"A-Staged"* when in this form. As the polymerization process is initiated (by the introduction of a catalyst, by an increase in temperature, or both), the molecular weight and viscosity increase rapidly. If the polymerization process is then halted in some manner (by suddenly reducing the temperature, say), the polymerization process will stop (or be dramatically slowed) and the polymer will exist in an intermediate stage. At this point the resin can be described as a very viscous fluid or very viscous solid, and contains molecules with perhaps 100 - 1000 repeat units. The thermoset resin is said to be *"B-Staged"* when in this form. Finally, if the polymerization process is allowed to continue until the maximum possible molecular weight has been reached, the thermoset is said to be *"C-Staged"*, i.e., the polymer is *fully polymerized*. Many thermoset adhesives are sold to the user in the form of a B-stage resin, usually as a thin film. The B-staged adhesive is both delivered to the user and stored (until needed) at low temperatures (at temperatures below about -18°C or 0°F, say). Refrigeration is required so that the thermosetting resin does not polymerize beyond the B-stage. The user completes the polymerization process (i.e., the resin is C-Staged) during final formation of an adhesive bond.

Both thermoplastic and thermoset polymers offer specific advantages and disadvantages. Generally speaking, thermoplastics are easiest to use in a production environment, because they can be melted and remelted many times. Thermosets are less easy to use because they must be stored under refrigeration and C-staged during the assembly or fabrication process. This often involves relatively complex, lengthy, and costly polymerization processes (also called *cure cycles*). Also, thermoplastics are often more ductile and tough than is the case with thermosets, which are important features from a structural standpoint.

On the other hand, many thermoplastics are easily *plasticized* by exposure to low-molecular weight *solvents*. Plasticization occurs when individual molecules of a low-molecular weight solvent (e.g., water, jet fuel, gasoline, or other hydrocarbons) is diffused into the polymeric molecular structure. Note that plasticization is defined at the molecular level - water *molecules* diffuse into the polymeric molecular structure, *not* water *droplets*. Conceptually, the small plasticizing molecule becomes "wedged between" the larger polymer molecule. The migration of relatively small solvent molecules within the surrounding polymer molecular structure causes an increase in the average molecular spacing, resulting in swelling of the polymer and a loss in stiffness and strength. In fact, fully-polymerized thermoplastics can be completely dissolved in a suitable solvent. Obviously, any thermoplastic considered for use in a load-bearing structural application must be carefully selected, with the potential service environment clearly defined. Also, the relatively low glass-transition temperature of many thermoplastics precludes their use in structural applications involving elevated temperatures (the glass transition temperature of a polymer is defined in section 1.9).

Thermosets are also susceptible to plasticization, and in fact lightly crosslinked rubbers will swell extensively if exposed to a suitable solvent. However, a polymerized thermoset cannot be completely dissolved, and the effects of plasticization are generally less pronounced than in the case of thermoplastics. Obviously, the factors just listed tend to favor the use of thermosets over thermoplastics in load-bearing structural applications.

1.7 Semicrystalline Polymers: The molecular structure of a polymer may be *amorphous* or *semicrystalline*. The molecular structure of an amorphous polymer is completely random; i.e., the molecular chains are randomly oriented and entangled, with no discernible pattern. In contrast, in a semicrystalline polymer there exist regions of highly ordered molecular arrays. An idealized representation of a crystalline region is shown in Figure 12. As indicated, in the crystalline region the main backbone of the molecular chain undulates back and forth such that the thickness of the crystalline region is usually (about) 100Å. The crystalline region may extend over an area with a length dimensions ranging from (about) 1,000 to 10,000 Å. Hence, the crystalline regions are typically plate-like. The high degree of order within the crystalline array allows for close molecular spacing, and hence high secondary bonding forces. At the macroscale a semicrystalline polymer typically has a higher strength, stiffness, and density than an otherwise comparable amorphous polymer.

To the authors knowledge no polymer is completely crystalline, however. Instead, regions of crystallinity are surrounded by amorphous regions, as shown schematically in Figure 13. Most semi-crystalline polymers are 10-50% amorphous (by volume).

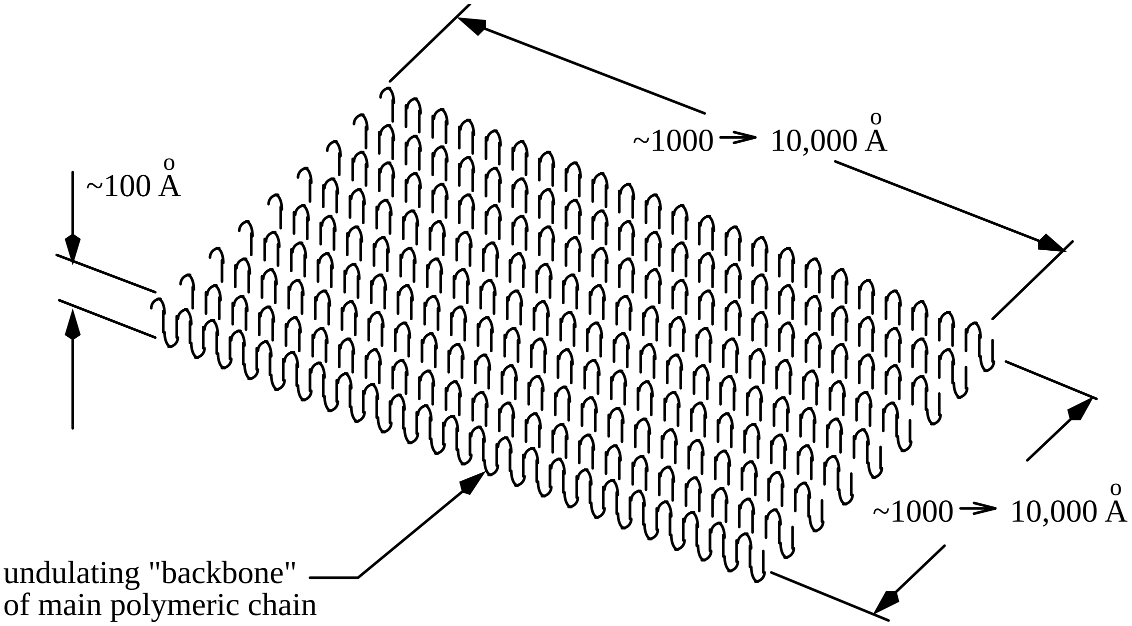


Figure 12: An idealized representation of a polymer crystalline region

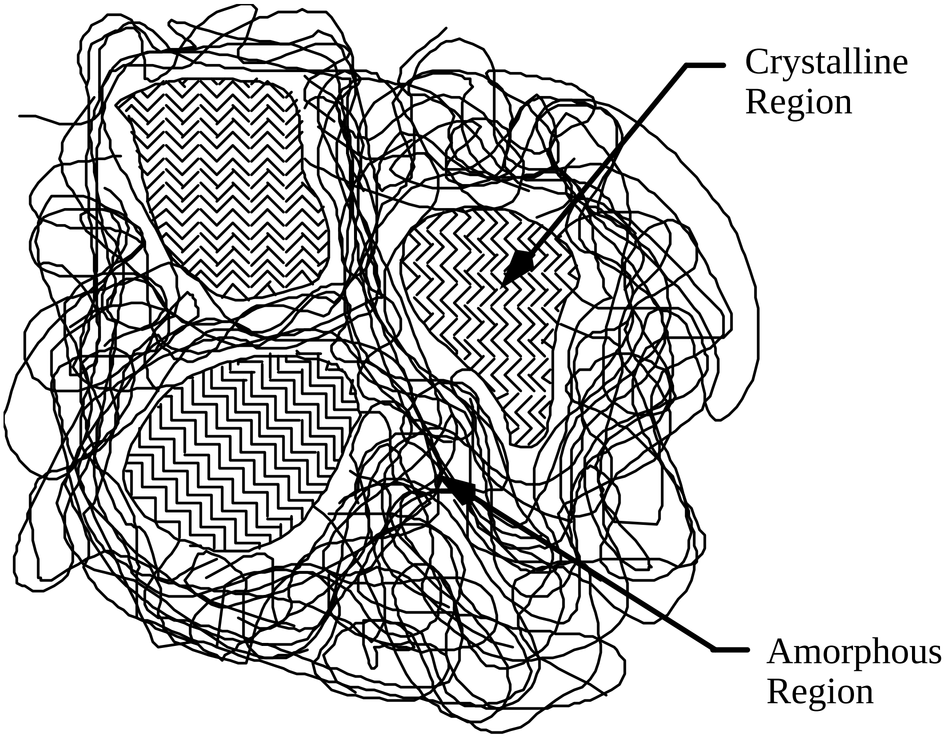
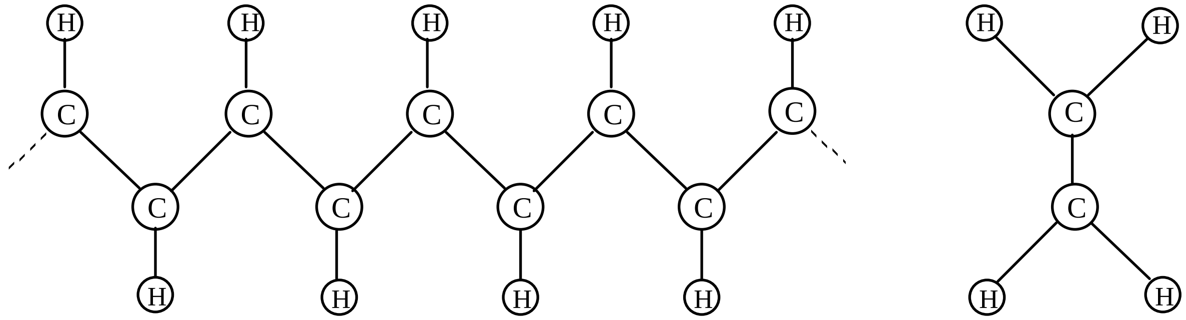


Figure 13: Overall molecular structure of a semicrystalline polymer, showing crystalline and amorphous regions.

1.8 Molecular "Conformation" vs "Configuration": As already discussed segments of an individual polymer molecule can rotate about covalent bonds. Such rotation occurs more-or-less continuously when the polymer is in a liquid state. Since these molecules are exceedingly "long" (on an atomic scale), even a slight rotation causes a gross change in the "global" shape of the molecule. Two terms are used to describe the "geometry" of a molecule: *conformation* and *configuration*.

Molecular *conformation* refers to atomic/molecular arrangements which can be developed strictly by rotation about covalent bonds, such as those shown in Figures 9 and 10, for example. Molecular conformations are associated with the "global" shape of the molecule - they can be thought of as a description of the molecular "macrostructure". Two extreme conformations are often discussed in the literature: the "planar zig-zag conformation" (or "extended chain conformation"), versus the "random coil" conformation. The planar zig-zag conformation and random coil conformations for polyethylene, are shown in Figures 14 and 15, for example. Note that the planar zig-zag conformation is strictly an idealization, and rarely (if ever) occurs in nature. On the other hand, a truly random coil conformation is also rare; there is usually some level of regularity, if over only short distances. Once again, molecular conformation is associated with the "macrostructure" of the molecule.

In contrast, molecular *configuration* is associated with local details - i.e., atomic/molecular arrangements that can only be developed by breaking, and then reforming, covalent bonds. Configurations as associated with the "microstructure" of the molecule. It is easiest to demonstrate



(a) “Side view”

(b) “End view”

Figure 14: Planar zig-zag conformation for polyethylene

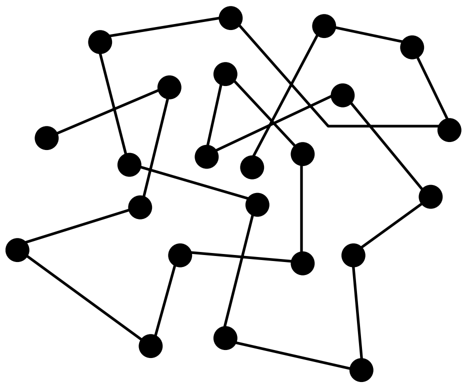
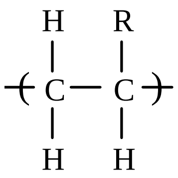


Figure 15: Random coil conformation for polyethylene (black dots represent carbon atoms; hydrogen atoms not shown)

various configurations based on the zig-zag conformation of a family of polymers known as "vinyls". The repeat unit of all vinyls can be represented as:



$$-\!\left(\begin{matrix} \mathrm{H} & & \mathrm{R} \\ | & & | \\ \mathrm{C} & - & \mathrm{C} \\ | & & | \\ \mathrm{H} & & \mathrm{H} \end{matrix}\right)\!-$$

where "R" may be one of several chemical entities[5]. Three potential configurations of a vinyl polymer are shown in Figures 16(a-c), where in each case the molecule is drawn using the zig-zag conformation. Note that the configuration shown in Figure 16(a) cannot be modified to match that of Figure 16(b) solely through rotation about covalent bonds.

Semicrystalline polymers are either syndiotactic or isotactic, since these molecular structures allow for the periodicity necessary in a crystalline polymer. Amorphous polymers, on the other hand, are usually atactic. In many cases the polymerization process used to create a bulk polymeric sample determines the configuration of the polymeric molecule, and hence ultimately determines whether the polymer is amorphous or semicrystalline.

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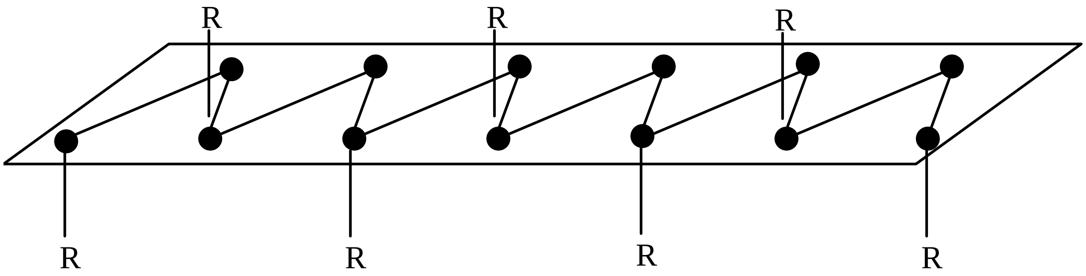
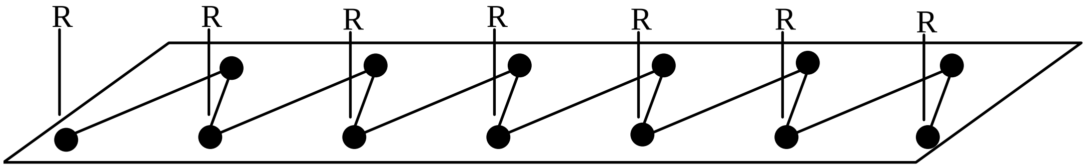
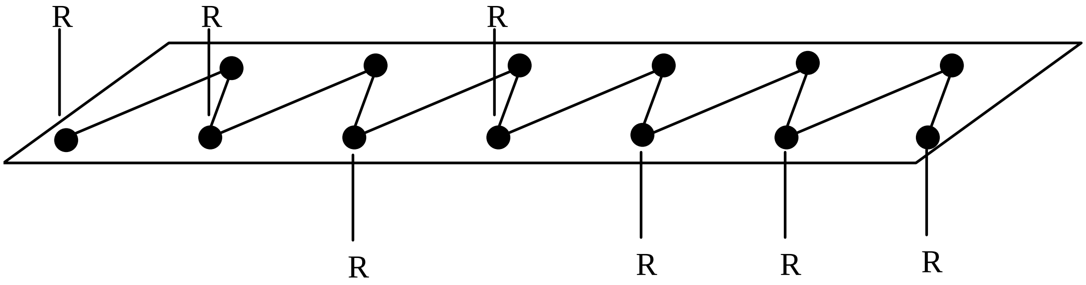
[5] For example, if "R" is a hydrogen atom, then the "vinyl" is polyethylene; i.e., polyethylene is a member of the vinyl family of polymers. Other members include polyvinylchloride (R = Cl), and polypropylene (R = CH_3).



(a) Syndiotactic configuration: R-unit appears on alternating sides of the planar zig-zag chain



(b) Isotactic configuration: R-units appear on same side of the planar zig-zag chain



(c) Atactic configuration: R-units appear randomly

Figure 16: Possible configurations for a vinyl polymer (black dots represent carbon atoms; hydrogen atoms not shown)

1.9 The Glass Transition Temperature: The effect of temperature on the macroscopic stiffness of both thermoplastic and thermoset polymers is shown schematically in Figure 17. Both types of polymers behave in a similar fashion, except that at high temperatures thermoplastics melt (modulus $\rightarrow 0$) whereas thermosets do not. Note that all polymers exhibit a decrease in stiffness near a characteristic temperature called the *glass-transition temperature*, T_g (occasionally the T_g is called the "alpha" transition temperature, T_α). For thermoplastics the decrease in stiffness may be *enormous* - 1-2 orders of magnitude. While a decrease also occurs for thermosets, typically the decrease is not so large. Roughly speaking, the T_g indicates the temperature at which the polymer is transformed from a relatively "glassy" and brittle solid to a relatively "rubbery" and ductile solid. This transition is due to an increase in mobility of large segments of the main polymeric chain. That is, when a polymer has been heated to the T_g the associated increase in average molecular spacing results in a sharp decrease in secondary bonding forces, allowing segments of the polymer molecules to each "slide" past each other. The glass transition typically occurs over a temperature range of 10-15°C.

Many polymers exhibit "secondary" transition temperatures, especially those with complex repeat units and/or branches. These secondary transitions occur at temperatures lower than the T_g, and are associated with other molecular mechanisms or motions, such rotation of a chain segment about a covalent bond. When multiple transition temperatures occur the highest transition temperature is called the "alpha" transition and the associated temperature the "alpha transition temperature" (and hence, $T_\alpha = T_g$), the next highest is called the "beta transition" (T_β), the next the "gamma" transition (T_γ), the next the "delta" transition (T_δ), etc, using ascending letters of the greek alphabet. A single secondary transition (T_β) has been shown in Figure 17.

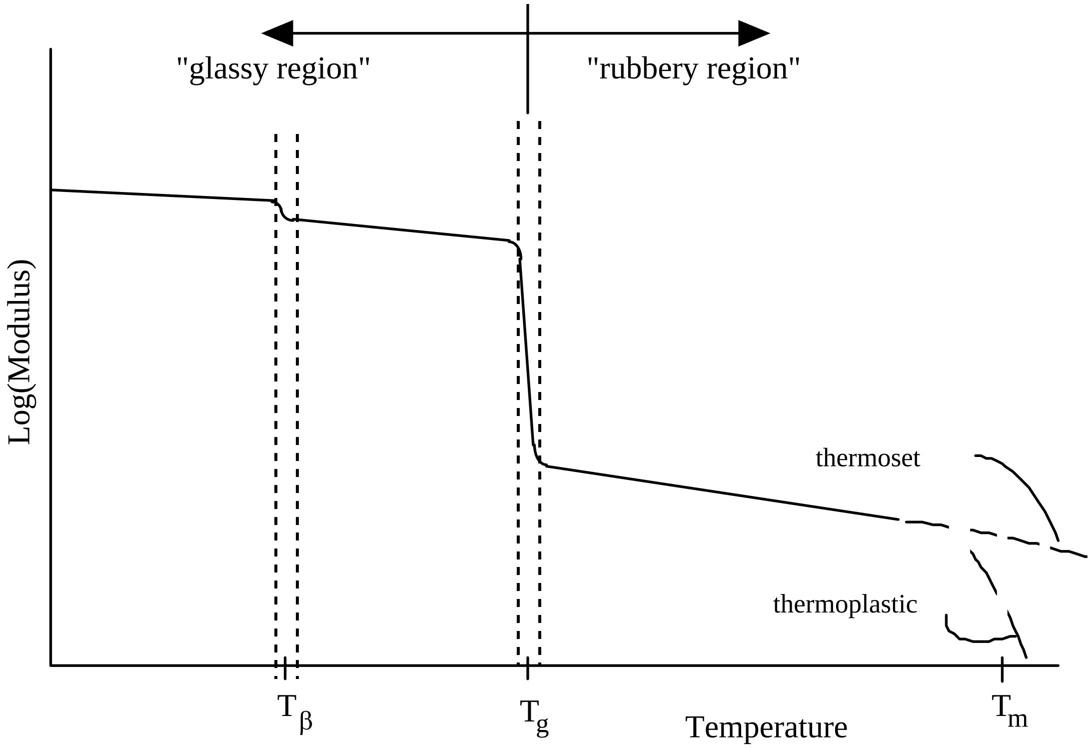


Figure 17: Effect of Temperature on the Macroscopic Stiffness of Polymers

At temperatures significantly below the T_g the polymer molecules are closely packed and tightly bonded by secondary bonding forces, and cannot easily slide past each other. The polymer is said to be in a "glassy" state at low temperatures, and exhibits a high stiffness and strength but (in general) low ductility. Conversely, at temperatures significantly above the T_g the molecular spacing is increased (and hence secondary forces are greatly decreased) such that large segments of molecular chains can more readily slide past each other. The polymer is said to be in a "rubbery" state at these higher temperatures, and exhibits a lower stiffness and strength but (in general) higher ductility.

The T_g exhibited by a few common polymers is listed in Table 3. Note that knowledge of the T_g allows an immediate assessment of the general nature of the polymer at room temperature. That is, a polymer with a very low T_g is "rubbery" and ductile at room temperatures, whereas a polymer with a very high T_g is "glassy" or "rigid" and brittle at room temperatures.

The preceding discussion of transition temperatures has been based on observed changes in stiffness. However, almost any physical property measured at the macroscopic level will exhibit a similar dependence on temperature. Thus, the T_g can be measured by monitoring polymer stiffness, density, thermal expansion, creep rate, etc.

Table 3: Approximate Glass Transition Temperatures for Some Common Polymers

Polymer	Typical Glass Transition Temperature		General Character at Room Temperatures
	°C	°F	
Silicone Rubber	-123	-190	Rubbery
Polybutadiene	-85	-120	Rubbery
Polyisoprene	-50	-60	Rubbery
Nylon 6/6	50	122	Rigid
Polyvinyl Chloride (PVC)	85	185	Rigid
Acrylonitrile-butadiene-styrene (ABS)	90	195	Rigid
Polystyrene	100	210	Rigid
Polyester	150	300	Glassy
Epoxy	175	350	Glassy
Polyetheretherketone (PEEK)	200	400	Glassy
Polyetherimide	215	420	Glassy

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