Chapter 12 (sections 12.4-12.8; additional homework problems)
Organic Chemicals, Functional Groups, and Polymers

**Functional groups**
Before you can understand polymer structure and function, you need to know a little bit of organic chemistry (the chemistry of carbon). The simplest type of organic compound is a hydrocarbon (contains only carbon and hydrogen) in which there are only single bonds. These are called alkanes. (You are supposed to know the names of straight chain alkanes containing from 1 to 10 carbon atoms.) C-C single bonds have very limited reactivity. The primary commercial uses of alkanes are as fuels or solvents. Most organic molecules consist of a structural backbone of C-C single bonds and one or more functional groups. Functional groups are portions of an organic molecule where carbon has bonds to atoms other than carbon or hydrogen.

<table>
<thead>
<tr>
<th>General formulas of class members</th>
<th>Class name</th>
<th>Typical compound</th>
<th>Compound name</th>
<th>Common use of sample compound</th>
</tr>
</thead>
<tbody>
<tr>
<td>R−X</td>
<td>Halide</td>
<td>H−C=−Cl</td>
<td>Dichloromethane (methylene chloride)</td>
<td>Solvent</td>
</tr>
<tr>
<td>R−OH</td>
<td>Alcohol</td>
<td>H−C=−OH</td>
<td>Methanol (wood alcohol)</td>
<td>Solvent</td>
</tr>
<tr>
<td>R−H</td>
<td>Aldehyde</td>
<td>H−C=−O</td>
<td>Methanal (formaldehyde)</td>
<td>Preservative</td>
</tr>
<tr>
<td>R−C−OH</td>
<td>Carboxylic acid</td>
<td>H−C=−C=−O</td>
<td>Ethanoic acid (acetic acid)</td>
<td>Vinegar</td>
</tr>
<tr>
<td>R−C−R'</td>
<td>Ketone</td>
<td>H−C=−C−H</td>
<td>Propanone (acetone)</td>
<td>Solvent</td>
</tr>
<tr>
<td>R−O−R'</td>
<td>Ether</td>
<td>C₃H₇−O−C₃H₇</td>
<td>Diethyl ether (ethyl ether)</td>
<td>Anesthetic</td>
</tr>
<tr>
<td>R−C−O−R'</td>
<td>Ester</td>
<td>CH₃C−O−C₂H₅</td>
<td>Ethyl ethanoate (ethyl acetate)</td>
<td>Solvent in fingernail polish</td>
</tr>
<tr>
<td>R−N</td>
<td>Amine</td>
<td>H−C=−N</td>
<td>Methylamine</td>
<td>Tanning hides (foul odor)</td>
</tr>
<tr>
<td>R−C−N−R'</td>
<td>Amide</td>
<td>CH₃C−N−H</td>
<td>Acetamide</td>
<td>Plasticizer</td>
</tr>
</tbody>
</table>

*R stands for an H or a hydrocarbon group such as −CH₃ or −C₆H₅. R' could be a different group from R.*

Compounds containing C=O group are called "carbonyl" compounds.
Condensation reaction of alcohols and carboxylic acids to form esters:

Esters generally smell sweet and are useful as flavoring agents, such as oil of wintergreen, and scents. The characteristic aroma of bananas is due to the ester prepared from acetic acid and the alcohol shown below (2-methylbutanol). Sulfuric acid is a catalyst for this reaction. Draw the structure of the products. (In the line drawings, a carbon is present at each vertex. Hydrogens attached to carbons are not shown.)

\[
\begin{align*}
\text{H}_2\text{SO}_4 & \quad \quad \text{H}_2\text{O} \\
\text{CH}_3\text{C} & \quad \quad \text{CH}_3 \\
\text{CH}_3 \quad \quad \text{CH}_3
\end{align*}
\]

What carboxylic acid and what alcohol would you combine to form acetylsalicylic acid (aspirin)?

Condensation reaction of amines and carboxylic acids to form amides:

Many of our most important polymers, such as proteins, are linked together with amide functional groups. Complete the following reactions:

\[
\begin{align*}
\text{CH}_3\text{C} & \quad \quad \text{CH}_3 \\
\text{CH}_3 \quad \quad \text{CH}_3
\end{align*}
\]

Why is the reverse reaction called a “hydrolysis” reaction?

Because water is used to break a bond.
Condensation reactions of alcohols to form ethers:

\[ 
\text{H}_3\text{C}-\text{CH}_2-\text{OH} + \text{HO}-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_3 + \text{H}_2\text{O} 
\]

\[ 
\text{H}_3\text{C} + \text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_3 \xrightarrow{\text{H}_2\text{SO}_4} \text{H}_3\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{CH}_3 
\]

You have been given the job of synthesizing MTBE, whose structure is shown below. (MTBE is an octane booster and is commonly added to gasoline during the winter months in states like Maryland, with high air pollution.) What two alcohols would you combine to prepare MTBE by a condensation reaction?

\[ 
\text{H}_3\text{C} = \text{O} \quad \text{H}_3\text{C} - \text{C} \quad \text{H}_3 \quad \text{H}_3 \quad \text{H}_3\text{C} - \text{O} - \text{C} - \text{CH}_3 
\]

Addition reactions of alkenes

The most common reactions of alkenes are addition reactions in which the double bond is converted to a single bond and two new bonds are formed.

Draw the structural formulas for the products of the following reactions:

- **Ethene**
  \[ 
  \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2 \rightarrow \text{H}_3\text{C} - \text{CH}_3 
  \]
  (The product is an alkane)

- **Ethene**
  \[ 
  \text{H}_2\text{C} = \text{CH}_2 + \text{H}_2\text{O} \rightarrow \text{H}_2\text{C} - \text{CH}_2\text{OH} 
  \]
  (The product is an alcohol)
Introduction to Polymers

A plastic soda bottle, a rubber band, nylon fishing line, a diaper, super glue, proteins, DNA, and RNA are all examples of polymers.

**Polymer:** A molecule of high molar mass formed by the joining of a large number of molecules of low molar mass.

**Monomer:** The small molecules that combine to form a polymer.

**Repeat unit:** The smallest group of atoms that appears throughout the entire polymer chain.

The formula for a polymer can be abbreviated: (repeat unit)$_n$ where $n$ is the number of repeats.

### Polymers of Commercial Importance

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
<th>Uses</th>
<th>Quantity $(10^9$ lb/yr)$^*$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition polymers:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyethylene</td>
<td>$\text{CH}_2-\text{CH}_2$</td>
<td>Films, packaging, bottles</td>
<td>23</td>
</tr>
<tr>
<td>Polypropylene</td>
<td>$\text{CH}_2-\text{CH}_2$</td>
<td>Kitchenware, fibers, appliances</td>
<td>9.5</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>$\text{CH}_2$</td>
<td>Packaging, disposable food containers, insulation</td>
<td>6.8</td>
</tr>
<tr>
<td>Polyvinyl chloride</td>
<td>$\text{CH}_2-\text{CH}_2$</td>
<td>Pipe fittings, clear film for meat packaging</td>
<td>11</td>
</tr>
<tr>
<td>Condensation polymers:</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polyurethane</td>
<td>$\text{R}-\text{NH}-\text{R}-\text{NH}-\text{C}-\text{O}^\cdot-\text{O}^\cdot$</td>
<td>&quot;Foam&quot; furniture stuffing, spray-on insulation, automotive parts, footwear, water-protective coatings</td>
<td>1.5</td>
</tr>
<tr>
<td>R, $R'$ = for example, $\text{-CH}_2-\text{-CH}_2$</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Polytetraethylene terephthalate</td>
<td>$\text{HO-CH}_2-\text{CH}_2-\text{O}^\cdot-\text{O}^\cdot$</td>
<td>Tire cord, magnetic tape, apparel, soft-drink bottles (all polyesters)</td>
<td>3.8</td>
</tr>
<tr>
<td>(a polyester)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Nylon 6,6</td>
<td>$\text{NH}+\text{CH}_2+\text{NH}^\cdot-\text{CH}_3$</td>
<td>Home furnishings, apparel, carpet fibers, fishing line (all nyons)</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*Source: Chemical and Engineering News, June 26, 1985, p. 42*
Polymerization reactions (condensation and addition)

Two common reactions used to synthesize polymers are addition reactions and condensation reactions.

**Addition polymerization**

Formed when an alkene adds to itself!

![Ethylene to Polyethylene](image)

High density polyethylene (HDPE) is composed of very long straight chains (~100,000 carbons!)
Low density polyethylene (LDPE) is composed of shorter chains with branches (~1000 carbons)

1. Write the abbreviated formula for polyethylene

\[
\left( \text{C}_2\text{H}_4 \right)_n
\]

See Table 12.6 for other addition polymers
Condensation polymerization

You have learned about the following condensation reactions:

Carboxylic acid + Alcohol = Ester + water
Carboxylic acid + Amine = Amide + water
Alcohol + Alcohol = Ether + water

Condensation polymers form from monomers that have at least two functional groups that can undergo a condensation reaction.

1. Write the formulas for the polymer that results from the following reactions (the first is a polyester, the second is a polyamide): (I also balanced the reactions)

\[ n \text{ HO-C-C-OH} + n \text{ HO-C-C-OH} \rightarrow \left( \text{C-C-C} - \text{C-C-C} - \text{C-C-C} \right)_n + (n-1) \text{H}_2\text{O} \]

\[ n \text{ HO-C-C-OH} + n \text{H}_2\text{N-C-C-NH}_2 \rightarrow \left( \text{C-N-C-N-C-N} \right)_n + (n-1) \text{H}_2\text{O} \]

2. Kevlar is a polymer with the following repeat unit:

\[ \text{add} \quad \left( \text{C} = \text{O} - \text{N} - \text{N} = \text{C} - \text{N} - \text{N} = \text{C} - \text{O} - \text{C} \right) \Rightarrow \text{add} \]

a. Kevlar is a polyamide

b. Write the structural formulas for the monomers used to synthesize kevlar.

\[ \text{dicarboxylic acid} \quad \text{diamine} \]
Kevlar is used for bullet-proof vests, rope, fire-resistant clothing, and sails. The strength of Kevlar comes from:

a. **Intramolecular Forces**: rigid aromatic (benzene) rings in the chains

b. **Intermolecular Forces**: hydrogen bonds between the chains

Circle the hydrogen bonds.
**Biopolymers**

**Proteins** are linear polymers of **amino acids**. Although there are (in theory) an infinite number of amino acids, only 20 different amino acids are commonly found in the proteins of all living organisms. Each amino acid differs only in the identity of the side chain. (See your textbook and the biopolymers handout for the structure of the 20 side chains.)

1. Draw the structure of a generic amino acid (use “R” to represent the side chain.)

   
   \[
   \begin{array}{c}
   \text{COOH} \\
   \text{H}_2\text{N} - \text{C} - \text{H} \\
   \text{R}
   \end{array}
   \]

   (positions of \( u \) groups altered to central carbon is not important for this course.)

2. Amino acids are connected through amide bonds (also called peptide bonds). Draw the structure of a generic dipeptide. (I've shown the entire condensation reaction.)

   \[
   \begin{array}{c}
   \text{H} \\
   \text{N}_2\text{N} - \text{C} - \text{C} - \text{H} \\
   \text{R}
   \end{array}
   \]

   \[
   + \begin{array}{c}
   \text{H} \\
   \text{N}_2\text{N} - \text{C} - \text{C} - \text{H} \\
   \text{R}'
   \end{array}
   \rightarrow \begin{array}{c}
   \text{H} \\
   \text{N}_2\text{N} - \text{C} - \text{C} - \text{N} - \text{C} - \text{C} - \text{H} \\
   \text{R} \quad \text{R}'
   \end{array}
   \]

3. The lengths of proteins can range from less than 50 to many thousands of amino acids. How many different proteins that are 100 amino acids long can be built from the 20 building blocks?

   \[
   \log x = 100 \log (20) = 130
   \]

   \[
   x = 10^{130}
   \]

   amide bond between two amino acids is also called a "peptide" bond. This is a dipeptide (2 amino acids)
Polysaccharides (complex carbohydrates) are polymers of sugars. Glucose (blood sugar) is stored inside animal cells in the form of a highly branched polymer called glycogen. (Plants store glucose in a very similar polymer called starch.) Glucose is one of the two major sources of cellular energy. When cells need glucose for energy, they can break down glycogen via hydrolysis.

(Each circle represents a glucose molecule)

1. Glucose can form a linear polymer in which carbon 1 of one molecule is linked to carbon 4 of another molecule through a “glycosidic bond”. A glycosidic bond looks exactly like an ether bond. Draw the structure of two glucose molecules linked through a 1-4 glycosidic bond.

2. The branches in glycogen are formed when carbon 1 of one molecule is linked to carbon 6 of another molecule through a 1-6 glycosidic bond.
   a. Why is carbon 1 always part of a glycosidic bond between two glucose molecules? (Look closely at the structure of glucose. What is different about carbon 1?)
      I'll let you think about this!
   b. If glucose was polymerized in a test tube using sulfuric acid as a catalyst, which carbons would be connected to carbon 1 through glycosidic bonds?
      Any one of the 6 carbons could be connected to carbon 1 (in cells, only carbons 4 or 6 are connected to carbon 1. This is due to the specificity of the enzymes that catalyze the reactions.)