INTRODUCTION TO BIOCHEMISTRY/POLYMERS

A STUDENT SHOULD BE ABLE TO:

1. With respect to lipids, identify:

   The characteristic common to members of the class (solubility in nonpolar solvents)
   The functional groups most important in triglycerides (triacylglycerols): Esters (and, in unsaturated fats, alkenes)
   The characteristic common to most naturally occurring fatty acids (even numbers of carbon atoms, cis configuration for unsaturated compounds, lack of branching)
   Saturated, unsaturated, and polyunsaturated fats; cis and trans fatty acids
   Characteristics that lead to higher melting points for fatty acids (saturation and higher molecular weight, trans over cis)
   The products (soap and glycerol) of saponification reactions given the triglyceride starting material, or vice versa

2. With respect to carbohydrates, identify:

   The approximate empirical formula characteristic of members of the class (CH₂O).
   The functional groups present in carbohydrate molecules: alcohols (usually several are present); aldehydes and ketones; hemiacetals and acetals
   Carbohydrates belonging to these classes: ketoses and aldoses; D and L sugars; polysaccharide classes (trioses, tetroses, pentoses, hexoses, etc.); α and β pyranoses; reducing and nonreducing sugars
   The products of oxidation and reduction reactions of carbohydrates (reducing sugars are those that can be oxidized. They contain hemiacetals (in the cyclic form) and aldehydes or ketones (in the straight chain form)
   The number of stereocenters in a carbohydrate given a Fisher structure

3. With respect to amino acids, polypeptides, and proteins, identify:

   The functional groups most important in these compounds. Proteins and polypeptides contain amides made from amino acid monomers; there are carboxylic acid and amine groups on the ends.
   The degree and site of protonation of amino acids as a function of pH
   Relative isoelectric points
   Polypeptide structures from N-terminal analysis, C-terminal analysis, and total and partial hydrolysis results

4. With respect to polymers, identify:

   Common monomer units and polymers made from them (ethylene, propylene, isobutylene, styrene and vinyl chloride.
   Recognize the following types of copolymers: alternating, random, block, and graft.
   Draw the mechanism for radical, cationic, anionic and condensation polymerizations
To best prepare for this module, please work suitable Chapters 24-27 Skill Builder problems in the textbook.

A STUDENT WHO HAS MASTERED THE OBJECTIVES ON THE PREVIOUS PAGE SHOULD BE ABLE TO SOLVE THE FOLLOWING PROBLEMS AND RELATED ONES:

1.1 In each of these pairs, which of the compounds has the higher melting point?
   a. CH$_3$(CH$_2$)$_{16}$COOH or CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH
   b. CH$_3$(CH$_2$)$_{14}$COOH or CH$_3$(CH$_2$)$_{16}$COOH

1.2 Which of the following fatty acids is a) saturated, b) monounsaturated, and c) polyunsaturated?
   A. CH$_3$(CH$_2$)$_{14}$COOH
   B. CH$_3$(CH$_2$)$_4$(CH=CHCH$_2$)$_4$(CH$_2$)$_2$COOH
   C. CH$_3$(CH$_2$)$_7$CH=CH(CH$_2$)$_7$COOH

1.3 a) Which of the following fatty acids is found commonly in cells?
   
   A. 
   B. 
   C. 
   D. 

   b) Identify each of the compounds in part (a) as cis, trans, or neither.

2.1 Identify each of the following sugars as either D or L.
   a) CH$_2$OH
   b) CHO
   c) CHO
   d) CH$_2$OH
2.2 For each of the structures below, provide the information needed to complete the table.

<table>
<thead>
<tr>
<th>Structure</th>
<th>Family</th>
<th>Backbone</th>
<th>Configuration</th>
<th>Number of Stereocenters</th>
</tr>
</thead>
<tbody>
<tr>
<td>a)</td>
<td>ketose</td>
<td>tetrose</td>
<td>D</td>
<td>1</td>
</tr>
<tr>
<td>b)</td>
<td></td>
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<td>c)</td>
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</tr>
<tr>
<td>d)</td>
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</tr>
<tr>
<td>e)</td>
<td></td>
<td></td>
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<td></td>
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</table>

2.3 a) Which of the disaccharides shown here gives a negative Tollens’ test (that is, does not give a silver mirror when treated with a solution of silver nitrate in aqueous ammonia)?

b) Why would heating the compound that is the answer to (a) with dilute aqueous acid yield a product that gives a positive Tollens’ test?
2.4 The structure of an important plant ketopentose, ribulose, is shown below. How many stereocenters does this molecule contain? Draw the structures of the other stereoisomers, and identify each as D or L.

\[
\begin{align*}
CH_2OH \\
\downarrow \\
C=O \\
H \quad OH \\
\downarrow \\
H \quad OH \\
CH_2OH
\end{align*}
\]

3.1 Based on the pK\textsubscript{a} values given, draw the dominant form of each of the following amino acids at pH 3, at pH 7, and at pH 13.

a) Glycine (structure below) has pK\textsubscript{a} values of 2.3 (for the $\alpha$-COOH) and 9.6 (for the $\alpha$-NH\textsubscript{3}\textsuperscript{+}).

\[
\text{glycine} \quad \text{pH 3} \quad \text{pH 7} \quad \text{pH 13}
\]

\[
\begin{align*}
\text{COOH} \\
H_2N \quad H \\
\downarrow \\
H
\end{align*}
\]

b) Glutamic acid, pK\textsubscript{a} values of 2.2, 9.7, and 4.3 (for the COOH group at the bottom).

\[
\text{glutamic acid} \quad \text{pH 3} \quad \text{pH 7} \quad \text{pH 13}
\]

\[
\begin{align*}
\text{COOH} \\
H_2N \quad H \\
\text{CH}_2 \\
\text{COOH}
\end{align*}
\]

c) Histidine, pK\textsubscript{a} values of 1.8, 9.2, and 6.0 (for the protonated N group on the ring).

\[
\text{histidine} \quad \text{pH 3} \quad \text{pH 7} \quad \text{pH 13}
\]

\[
\begin{align*}
\text{COOH} \\
H_2N \quad H \\
\text{CH}_2 \\
\text{NH}
\end{align*}
\]
3.2. A pentapeptide was completely hydrolyzed and found to contain aspartic acid (Asp), lysine (Lys), proline (Pro), and methionine (Met). After partial hydrolysis the dipeptides Lys-Asp, Met-Pro, Lys-Met, and Pro-Lys were identified in the product. What is the sequence of amino acids in this pentapeptide?

A. Lys-Met-Pro-Lys-Asp  
B. Asp-Lys-Pro-Met-Lys  
C. Lys-Asp-Met-Pro-Lys  
D. Pro-Met-Lys-Pro-Asp

3.3 A tridecapeptide (an oligopeptide with 13 amino acid residues) has the following amino acid composition: Ala, Arg, Asp2, Glu2, Gly3, Leu, and Val3. After partial acid hydrolysis of the tridecapeptide, the following peptides were isolated, and their sequences were determined by Erdman degradation. What is the sequence of the original tridecapeptide?

The peptides are:
Asp-Glu-Val-Gly-Gly-Glu-Ala  
Val-Asp-Val-Asp-Glu  
Val-Asp-Val  
Glu-Ala-Leu-Gly-Arg  
Val-Gly-Gly-Glu-Ala-Leu-Gly-Arg  
Leu-Gly-Arg

4.1 Name the following monomers or polymers

4.2 Classify the following copolymer and identify the monomer units

4.3 Propylene polymerizes via cationic polymerization in the presence of HCl. Show the mechanism for this reaction including initiation, propagation and termination steps.
SOLUTIONS TO SAMPLE PROBLEMS:

1.1 a) CH₃(CH₂)₁₆COOH  b) CH₃(CH₂)₁₆COOH

1.2 a) A  b) C  c) B

1.3 a) B  b) B and D are cis, C is trans, and A is neither cis nor trans.

2.1 a) D  b) L  c) D  d) L

2.2 Structure  Family  Backbone  Configuration  Number of Stereocenters

<p>| | | | | |</p>
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<td>hexose</td>
<td>D</td>
<td>3</td>
</tr>
<tr>
<td>c</td>
<td>aldose</td>
<td>hexose</td>
<td>L</td>
<td>4</td>
</tr>
<tr>
<td>d</td>
<td>ketose</td>
<td>triose</td>
<td>none</td>
<td>0</td>
</tr>
<tr>
<td>e</td>
<td>aldose</td>
<td>pentose</td>
<td>D</td>
<td>3</td>
</tr>
</tbody>
</table>

2.3 a) Sucrose. The negative Tollens’ test indicates that the compound is not a reducing sugar; sucrose does not contain a hemiacetal, and therefore is not a reducing sugar. Lactose would give a positive Tollens’ test due to the hemiacetal functional group contained in the structure.

b) Warming with dilute aqueous acid hydrolyzes sucrose into two monosaccharides by cleaving the acetal linkage. It would then produce hemiacetal groups on each of the monosaccharides and thus they become reducing sugars.

2.4 Ribulose contains two stereocenters. The structures of the isomers are:

\[
\begin{align*}
\text{ribulose} & : \quad \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{C}=\text{O} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{CH}_2\text{OH} \\
\text{D}
\end{array} & \quad \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{C}=\text{O} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{CH}_2\text{OH} \\
\text{D}
\end{array} & \quad \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{C}=\text{O} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{CH}_2\text{OH} \\
\text{L}
\end{array} & \quad \begin{array}{c}
\text{CH}_2\text{OH} \\
\text{C}=\text{O} \\
\text{H} \quad \text{OH} \\
\text{H} \quad \text{OH} \\
\text{CH}_2\text{OH} \\
\text{L}
\end{array}
\end{align*}
\]
3.1 a) Glycine, pK\textsubscript{a} values of 2.4 and 9.8. If the pK\textsubscript{a} value for a given proton is less than the pH, that proton is removed.

\[\text{glycine} \quad \text{pH 3} \quad \text{pH 7} \quad \text{pH 13}\]

\[
\begin{align*}
\text{COOH} & \quad \text{COO}^- \\
\text{H}_2\text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

b) Glutamic acid:

\[\text{glutamic acid} \quad \text{pH 3} \quad \text{pH 7} \quad \text{pH 13}\]

\[
\begin{align*}
\text{COOH} & \quad \text{COO}^- \\
\text{H}_2\text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{(CH}_2\text{)}_2 & \quad \text{(CH}_2\text{)}_2 \\
\text{COOH} & \quad \text{COO}^- \\
\end{align*}
\]

c) Histidine:

\[\text{histidine} \quad \text{pH 3} \quad \text{pH 7} \quad \text{pH 13}\]

\[
\begin{align*}
\text{COOH} & \quad \text{COO}^- \\
\text{H}_2\text{N} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{CH}_2 & \quad \text{CH}_2 \\
\end{align*}
\]

3.2 A

3.3 Val-Asp-Val-Asp-Glu-Val-Gly-Gly-Glu-Ala-Leu-Gly-Arg

4.1 isobutylene, polyvinylchloride

4.2 Alternating copolymer made from propylene and styrene
Initiation (this is an electrophilic addition)

Propagation (this is also like an electrophilic addition)

Termination (This is like the second step on an E1)
1. What is the structure of the amino acid HO\(_2\)CCH\(_2\)CH(NH\(_2\))COOH at a pH of 2.5? The pK\(_a\)'s are 2.2, 9.7, and 4.3 (for the second COOH).

   A. H\(_2\)NCHCO\(_2\)\(^-\)  B. H\(_3\)NCHCO\(_2\)\(^-\)  C. H\(_3\)NCHCO\(_2\)H  D. H\(_2\)NCHCO\(_2\)\(^-\)

\[ \text{CH}_2\text{CO}_2\text{H} \quad \text{CH}_2\text{CO}_2\text{H} \quad \text{CH}_2\text{CO}_2\text{H} \quad \text{CH}_2\text{CO}_2\text{H} \]

2. Which of the following functional groups is NOT present in the molecule shown?

   A. Acetal  B. Hemiacetal  C. 1\(^\circ\) Alcohol  D. 2\(^\circ\) Alcohol

3. What functional group is most abundant in proteins?

   A. Amide  B. Amine  C. Carboxylic acid  D. Alcohol

4. What are the major products of the reaction shown?

   \[ \text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2 \quad \text{NaOH, excess} \quad \text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2 \quad \text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{CH}_2 \]

   I: \(\text{CH}_2-\text{CH}-\text{CH}_2\)  II: \(\text{CH}_2-\text{CH}—\text{CH}_2\)  III: \(\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{H}\)

   | OH | OH | OH | ONa | ONa | ONa |

   IV: \(\text{CH}_3(\text{CH}_2)_{12}\text{CO}_2\text{Na}\)

   A. I and III  B. I and IV  C. II and III  D. II and IV

5. The structure of ribose is shown. Ribose is a (an):

   A. Aldopentose  B. Aldohexose  C. Ketopentose  D. Ketohexose

6. Draw the structure of polystyrene
1. Complete the following equation. Give all organic products.

\[ \text{CH}_2\text{O}_2\text{C(CH}_2\text{)}_{12}\text{CH}_3 \]

\[ | \]

\[ \text{NaOH, excess} \]

\[ \text{CHO}_2\text{C(CH}_2\text{)}_{12}\text{CH}_3 \]

\[ \rightarrow ? \]

\[ | \]

\[ \text{CH}_2\text{O}_2\text{C(CH}_2\text{)}_{12}\text{CH}_3 \]

2. Which of the compounds below does NOT give a red precipitate with Benedict’s reagent?

(A) ![Compound A]

(B) ![Compound B]

(C) ![Compound C]

(D) ![Compound D]

3. What is the structure of the amino acid shown at a pH of 12? The pKa’s are 2.2 (COOH), 9.0 (NH$_2$), and 10.5 (side chain NH$_2$).

\[ \text{H}_2\text{N} - \text{C} - \text{CO}_2\text{H} \]

\[ \text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2 \]

4. An oligopeptide was analyzed and found to contain the amino acids Phe, Cys, Ala, Ile, Asp, Trp, Thr, and Arg. N-terminal analysis identified Phe, and C-terminal analysis gave Ile. The fragments Arg-Ala-Ile, Cys-Asp-Arg, and Trp-Thr-Cys were identified after partial hydrolysis. What is the amino acid sequence of this peptide?

5. Give the general structure of a block copolymer using monomers A and B