Cellulose: the Basics

- Linear polymer made up of β-d glucopyranose units linked with 1→4 glycosidic bonds.
- Repeating unit = glucose (cellobiose)
- Glucopyranose units in chair form - most thermodynamically stable. Only 2% in other forms
- CH₂OH and OH groups in equatorial positions → stability

Cellulose: More Basics

- Cellulose is elongated and the glucose units in one plane for the following reasons:
  - β 1→4 linkages
  - The thermodynamic stability of the chair form
  - The positioning of the groups on the ring: E versus Al
- Amylose (starch) occurs as a helix in solid state because of the α 1→4 linkage.

Reducing End Groups

- Each cellulose chain has 1 reducing end group at the C1 position of the terminal glucopyranose unit
- The C4 position of the other terminal unit is an alcohol and therefore non-reducing.
- Does the reducing end mutarotate?
  - In fibers, probably not because of hydrogen bonding, etc.
  - In solution, probably
**Cellulose: Molecular Weight**

Degree of Polymerization of Cellulose

\[ \text{DP} = \frac{\text{molecular weight of cellulose}}{\text{molecular weight of one glucose unit}} \]

- Determination of molecular weight requires isolation and solubilization of cellulose
- Isolation procedures will modify (reduce) molecular weight
- Various modification procedures used for isolation
  - Derivatize with a variety of agents
  - Metal complexes
  - Pulping
  - Solvent systems

**Degree of Polymerization**

<table>
<thead>
<tr>
<th>Material</th>
<th>Degree of polymerization</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cotton (unopened)</td>
<td>15,300</td>
</tr>
<tr>
<td>Aspen (Hardwood)</td>
<td>10,300</td>
</tr>
<tr>
<td>Jack Pine (Softwood)</td>
<td>7900</td>
</tr>
<tr>
<td>Bacteria</td>
<td>5000</td>
</tr>
<tr>
<td>Sulfite pulp, bleached</td>
<td>1255</td>
</tr>
<tr>
<td>Kraft pulp</td>
<td>975</td>
</tr>
<tr>
<td>Rayon</td>
<td>305</td>
</tr>
</tbody>
</table>

**Molecular Weight**

- Determination of the molecular weight of the glucose molecule on the left is quite simple.
- Simply count all of the atoms and add up the molecular weight.

![Glucose molecule](image)

<table>
<thead>
<tr>
<th>Carbons</th>
<th>Oxygen</th>
<th>Hydrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>6 x 12</td>
<td>6 x 16</td>
<td>12 x 1</td>
</tr>
<tr>
<td>72</td>
<td>96</td>
<td>12</td>
</tr>
<tr>
<td>180 g/mole</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Molecular Weight of Mixtures**

- What if you have a mixture of 4 different chemicals and refer to it as a single compound like cellulose. What is the molecular weight?

![Molecule with different units](image)

<table>
<thead>
<tr>
<th>180 g/mole</th>
<th>342 g/mole</th>
<th>504 g/mole</th>
<th>660 g/mole</th>
</tr>
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</tr>
</tbody>
</table>
The simple answer to the question of molecular weight of mixtures is that you use an average of the molecular weights. This is known as the number average molecular weight.

\[
M_n = \frac{\sum N_x M_x}{\sum N_x}
\]

Although this gives a number which is usable, it doesn’t completely describe the system. This is because you can obtain the same number average molecular weight with completely different mixtures. For example, a sample of all medium sized molecules and a mixture of big and little molecules could give the same value.

The second method for determining molecular weight is the weight average method. This method gives values which are influenced by the amount of larger molecules. This equation is developed from the number average equation by replacing the number of molecules \(N_x\) by the weight of the molecules \(C_x\). For examples on calculating molecular weight, see the end of this lecture.

\[
M_w = \frac{\sum C_x M_x}{\sum C_x} = \frac{\sum N_x M_x / M_x}{\sum N_x M_x} = \frac{\sum N_x \Delta M_x}{\sum N_x M_x}
\]

Polydispersity is the ratio of the weight average molecular weight to the number average molecular weight. This value provides information on the distribution of molecular weights. Larger values indicate that you have a wide range of molecular weights while low values mean a narrow distribution.

\[
\text{Polydispersity} = \frac{M_w}{M_n}
\]
Molecular Weight Determination Methods

- Number Average (Mn)
  - Osmometry
  - Reducing end group analysis (cellulose)
- Weight Average (Mw)
  - Light Scattering
- Others: Mz and Mv
  - Ultracentrifugation
  - Viscosity Measurements

Example Problems

Cellulose

1. Number Average Mn
   \[ M_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{(5)(1) + (5)(5) + (5)(10)}{5+5+5} = 5.33 \]

2. Weight Average Mw
   \[ M_w = \frac{\sum C_x M_x}{\sum C_x} = \frac{(5)(1)(1) + (5)(5)(5) + (5)(10)(10)}{(5)(1) + (5)(5) + (5)(10)} = 7.875 \]

3. Polydispersity
   \[ P.D. = \frac{M_w}{M_n} = 1.477 \]
Cellulose
Molecular Weight: Example 2

1. Number Average Mn
Mn = \frac{\sum NxMx}{\sum N} = \frac{(25)(1) + (5)(5) + (5)(10)}{25 + 5 + 5} = 2.86

2. Weight Average Mw
Mw = \frac{\sum CxMx}{\sum Cx} = \frac{(25)(1) + (5)(5)^2 + (5)(10)^2}{(25)(1) + (5)(5) + (5)(10)} = 6.50

3. Polydispersity
= \frac{Mw}{Mn} = 2.27

Cellulose
Molecular Weight: Example 3

1. Number Average Mn
Mn = \frac{\sum NxMx}{\sum N} = \frac{(5)(1) + (25)(5) + (5)(10)}{5 + 25 + 5} = 5.14

2. Weight Average Mw
Mw = \frac{\sum CxMx}{\sum Cx} = \frac{(5)(1) + (25)(5)^2 + (5)(10)^2}{(5)(1) + (25)(5) + (5)(10)} = 6.27

3. Polydispersity
= \frac{Mw}{Mn} = 1.22
1. Number Average $M_n$

$$M_n = \frac{\sum N_x M_x}{\sum N_x} = \frac{(5)(1) + (5)(5) + (25)(10)}{5+5+25} = 8.00$$

2. Weight Average $M_w$

$$M_w = \frac{\sum C_x M_x}{\sum C_x} = \frac{(5)(1)(1) + (5)(5) + (25)(10)^2}{(5)(1) + (5)(5) + (25)(10)} = 9.39$$

3. Polydispersity

$$\frac{M_w}{M_n} = 1.17$$