Wood Chemistry

Wood Chemistry

PSE 406 / Chem E 470

Lecture 5

Cellulose

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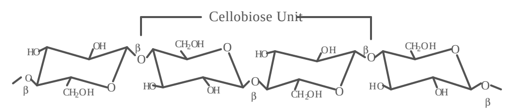
Cellulose: the Basics

- 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
- CH_2OH and OH groups in equatorial positions → stability



Cellulose

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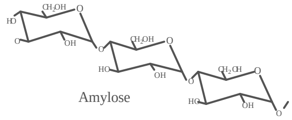
Cellulose: More Basics

- 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.



Amylose

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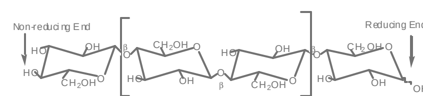
Reducing End Groups

- 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 not reducing.
- Does the reducing end mutarotate?
  - » In fibers, probably not because of hydrogen bonding, etc.
  - » In solution, probably



Notes

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Cellulose: Molecular Weight

Degree of Polymerization of Cellulose

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

- 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

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Degree of Polymerization

Material	Degree of polymerization
Cotton (unopened)	15,300
Aspen (Hardwood)	10,300
Jack Pine (Softwood)	7900
Bacteria	5000
Sulfite pulp, bleached	1255
Kraft pulp	975
Rayon	305

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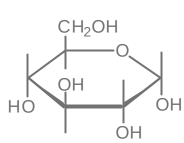
Molecular Weight Determination

- 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.



Carbons	6 x 12 = 72
Oxygen	6 x 16 = 96
Hydrogen	12 x 1 = 12

180 g/mole

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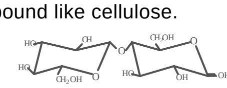
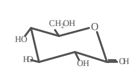
Molecular Weight of Mixtures

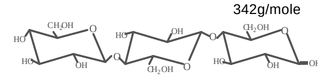
- What if you have a mixture of 4 different chemicals and refer to it as a single compound like cellulose. What is the molecular weight?



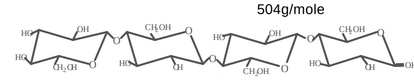
342g/mole



180g/mole



504g/mole



666g/mole

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Molecular Weight of Mixtures

- 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.

Number Average Molecular Weight (Mn)

$$Mn = \frac{\text{weight}}{\text{\# molecules}} = \frac{\sum NxMx}{\sum Nx}$$

- 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 mixtures of big and little molecules could give the same value.

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Molecular Weight Equations

- 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 Nx by the weight of the molecules Cx. For examples on calculating molecular weight, see the end of this lecture.

Weight Average Molecular Weight (Mw)

$$Mw = \frac{\sum CxMx}{\sum Cx} = \frac{\sum (NxMx)(Mx)}{\sum NxMx} = \frac{\sum NxMx^2}{\sum NxMx}$$

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Polydispersity

- 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.

Polydispersity

Polydispersity = Mw/Mn

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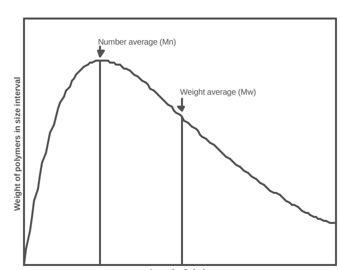
Molecular Weight Distribution



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Molecular Weight Determination Methods

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

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Example Problems

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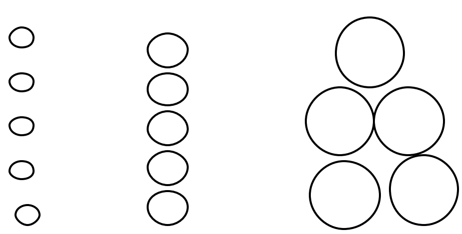
Molecular Weight: Example 1



1g/mole 5g/mole 10 g/mole

Note: These values represent the molecular weight of each of spheres

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Cellulose Molecular Weight: Example 1

1. Number Average Mn

$$Mn = \frac{\sum NxMx}{\sum Nx} = \frac{(5)(1) + (5)(5) + (5)(10)}{5+5+5} = 5.33$$

2. Weight Average Mw

$$Mw = \frac{\sum CxMx}{\sum Cx} = \frac{(5)(1)(1) + (5)(5)^2 + (5)(10)^2}{(5)(1) + (5)(5) + (5)(10)} = 7.875$$

3. Polydispersity

$$= \frac{Mw}{Mn} = 1.477$$

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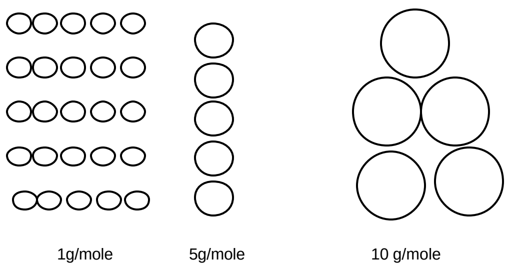
Cellulose
Molecular Weight: Example 2



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Cellulose
Molecular Weight: Example 2

1. Number Average Mn

$$Mn = \frac{\sum NxMx}{\sum Nx} = \frac{(25)(1) + (5)(5) + (5)(10)}{25+5+5} = \mathbf{2.86}$$

2. Weight Average Mw

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

3. Polydispersity

$$= \frac{Mw}{Mn} = 2.27$$

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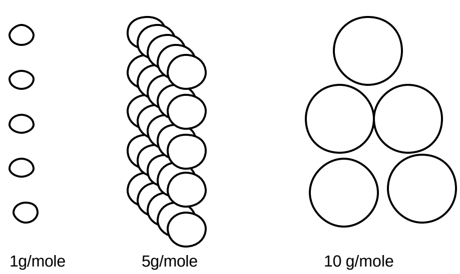
Cellulose
Molecular Weight: Example 3



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Cellulose
Molecular Weight: Example 3

1. Number Average Mn

$$Mn = \frac{\sum NxMx}{\sum Nx} = \frac{(5)(1) + (25)(5) + (5)(10)}{5+25+5} = 5.14$$

2. Weight Average Mw

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

3. Polydispersity

$$= \frac{Mw}{Mn} = 1.22$$

Cellulose

Molecular Weight: Example 4

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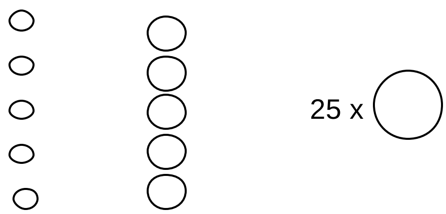

1g/mole   5g/mole   10 g/mole

Cellulose

Molecular Weight: Example 4

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1. Number Average Mn

$$Mn = \frac{\sum NxMx}{\sum Nx} = \frac{(5)(1) + (5)(5) + (25)(10)}{5+5+25} = \mathbf{8.00}$$

2. Weight Average Mw

$$Mw = \frac{\sum CxMx}{\sum Cx} = \frac{(5)(1)(1) + (5)(5)^2 + (25)(10)^2}{(5)(1) + (5)(5) + (25)(10)} = 9.39$$

3. Polydispersity

$$= \frac{Mw}{Mn} = 1.17$$