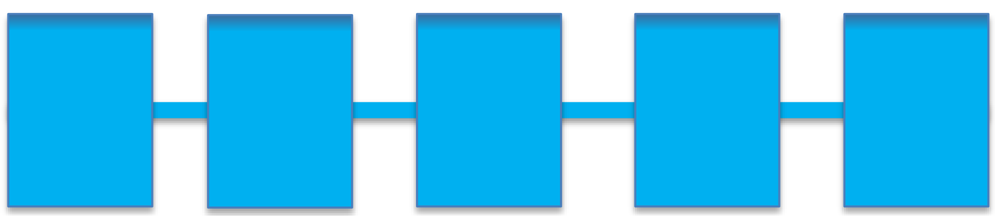
Lecture 3

Getting tangled up

Polymers (AKA) Macromolecules

- Large molecules composed of “simple” repeat units that are covalently bonded to each other
  - Derived from **monomers**
  - A few monomers linked together is an oligomer
- Large molecules have many potential **intermolecular interactions** sites
  - contrast small alkanes to paraffin wax to polyethylene



Other views of polymers

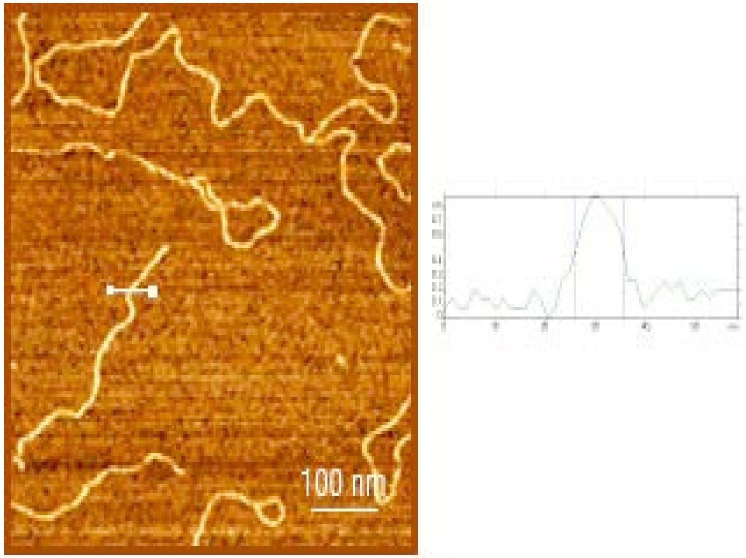


Image courtesy of S. Magonov, Agilent Technologies. http://www.spmtips.com/how-to-choose-afm-probes-by-resolution-general-purpose.html

Polymers are the big kids on the block in the atomic/molecular world

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Analogy: Sugar cubes (glucose) vs. ropes (cellulose and starch)

Image– thebotu

Image-- Jelks Coffee

Small molecules → (Polymerization) → Polymers

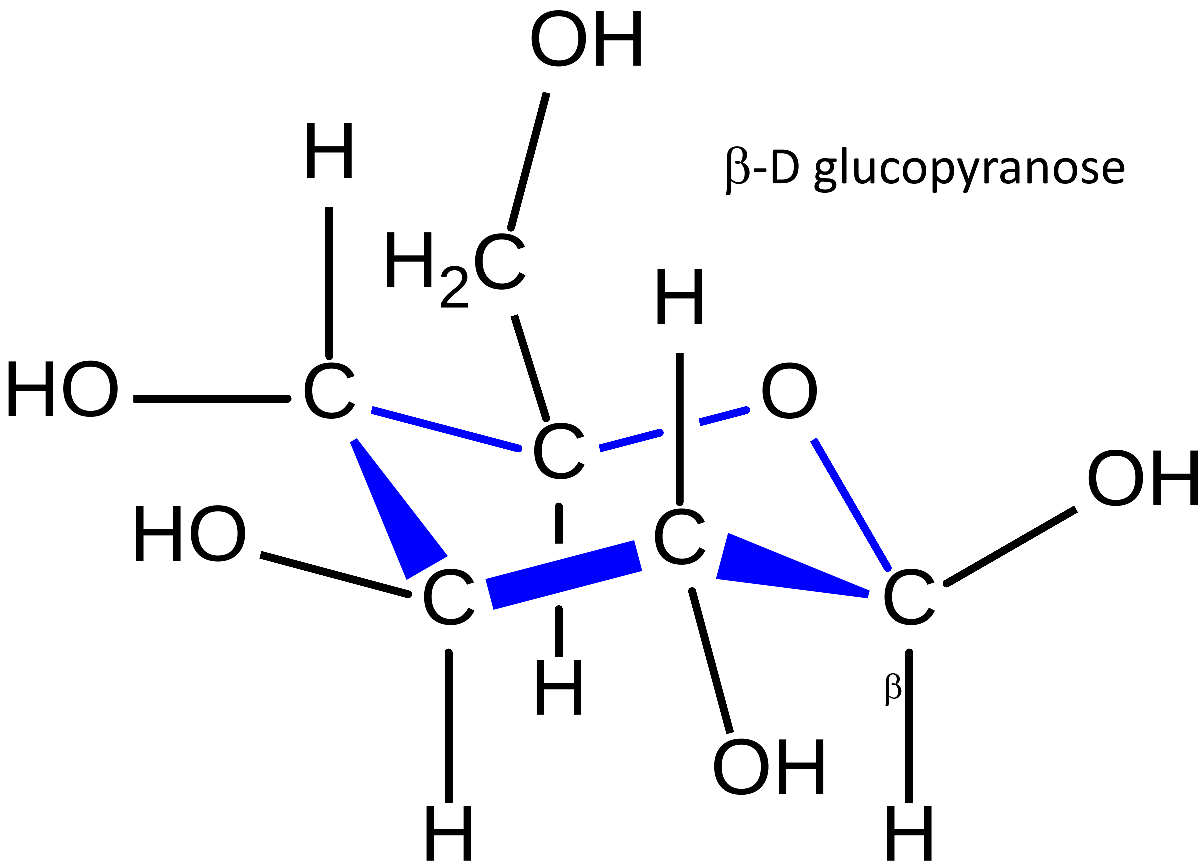
- Chemical Composition
- Topology
- Morphology
- Molecular weight (degree of polymerization)
- Additives/plasticizers (H_2O for biopolymers)

Plants commonly make two forms of polymers directly from glucose: starch and cellulose

- Cellulose is known as a **structural polymer** for plants
  - Must meet demanding mechanical performance for plant survival
- Starch is known as a **energy reserve polymer** for plants
  - Must have some reversible nature to “unzip” back into glucose.
- Difference in materials:
  - α-linkage in starch allows backbone to bend
  - β-linkage causes backbone to remain straight. This structural difference **leads to major property differences**.

Polymer chemistry can be used to help understand differences in performance because of this simple difference

Glucose shown in chair form: product from photosynthesis



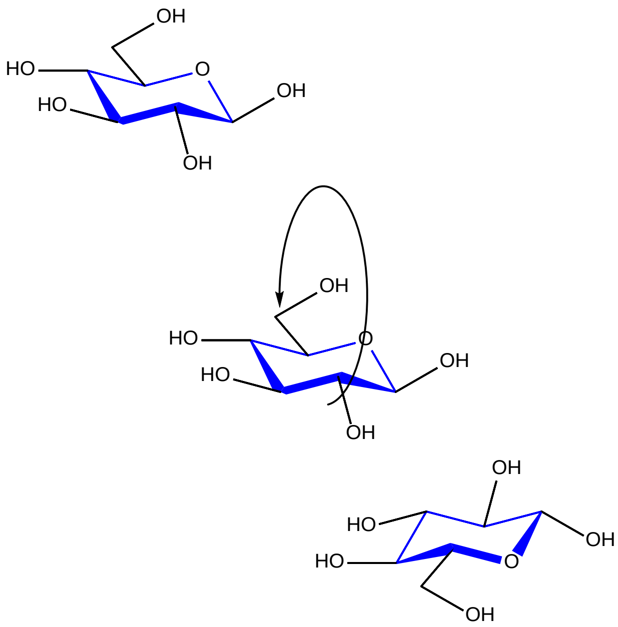
β-D glucopyranose

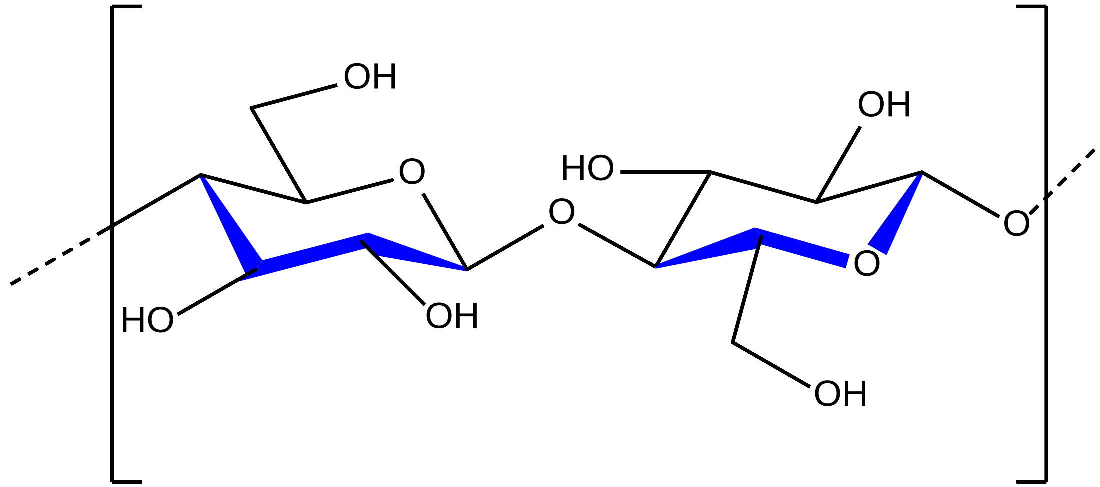
Pyranose ring

Terminology to know
- Axial
- Equatorial

Also be able to label C1 to C6 carbons

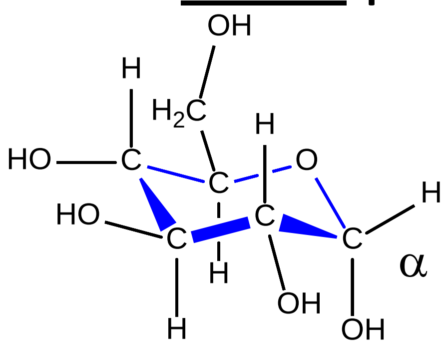
Two glucose units together = cellobiose

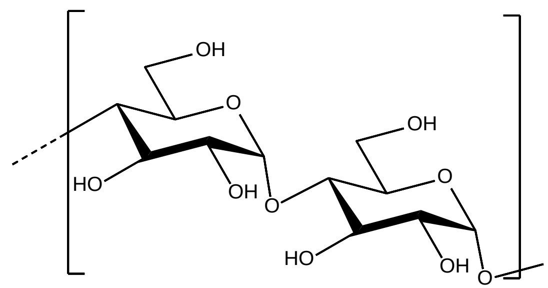




In contrast, Let's look at starch

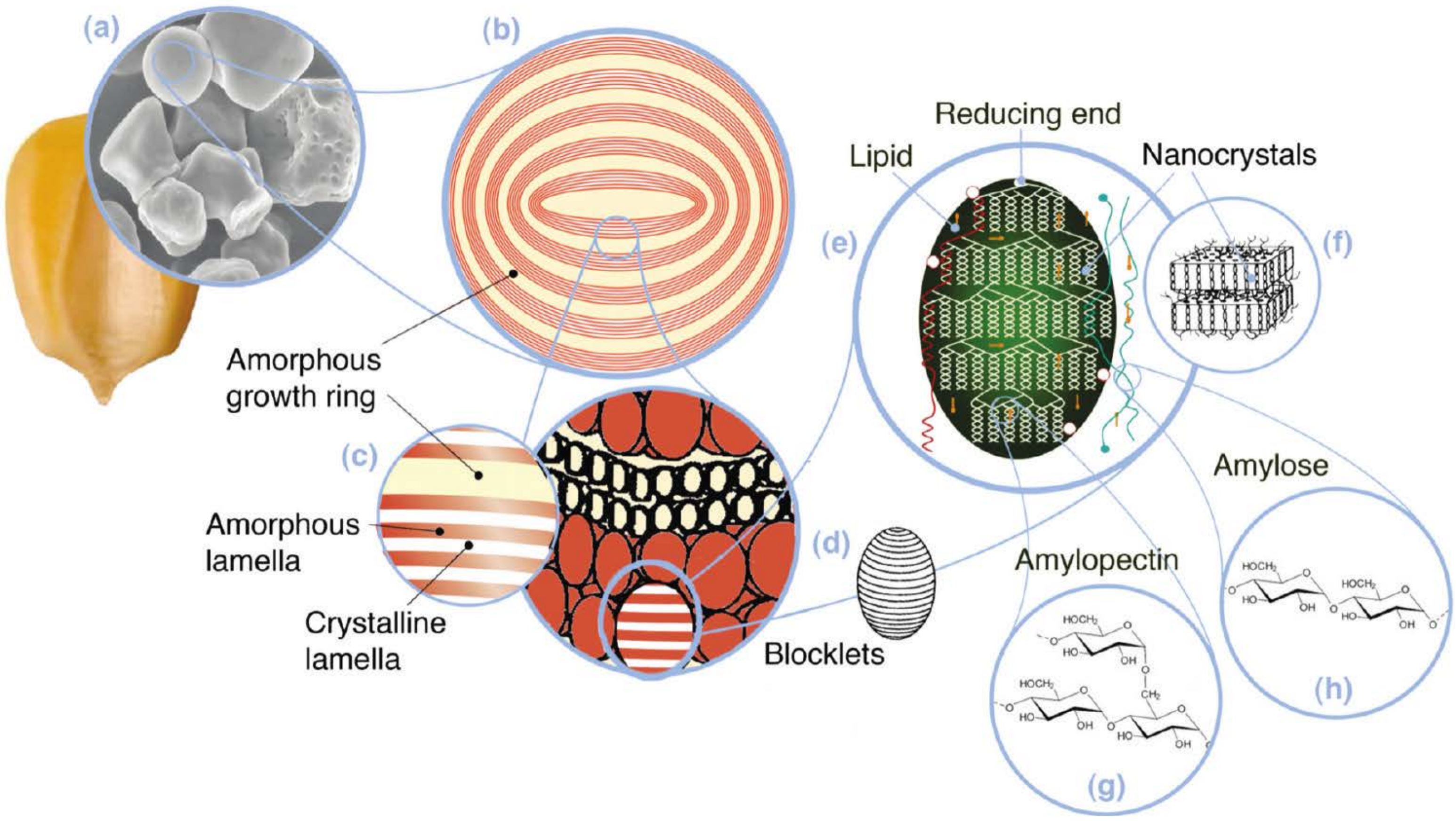
- Starch is composed of two biopolymers
  - **Amylose and amylopectin**
- **Amylose** is a <u>*linear*</u> polymer of α 1-4 linked glucose units



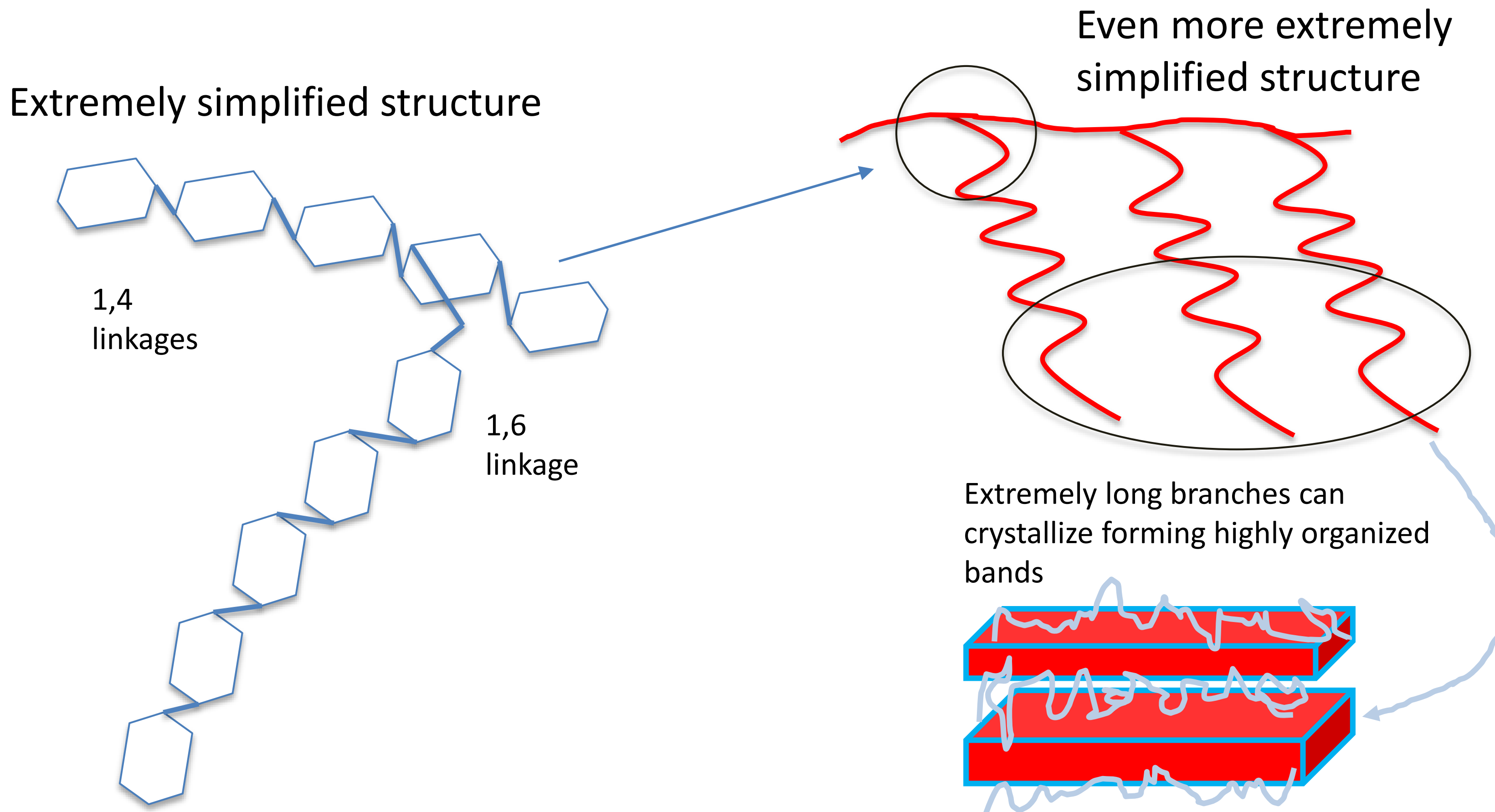


- **Amylopectin** is a <u>*branched*</u> polymer of α 1-4 linked glucose units but also has **branches** linked at α 1-6.
  - Amylopectin is one of the only "branched" polymers that has crystallinity because the branches are so long

Starch structure

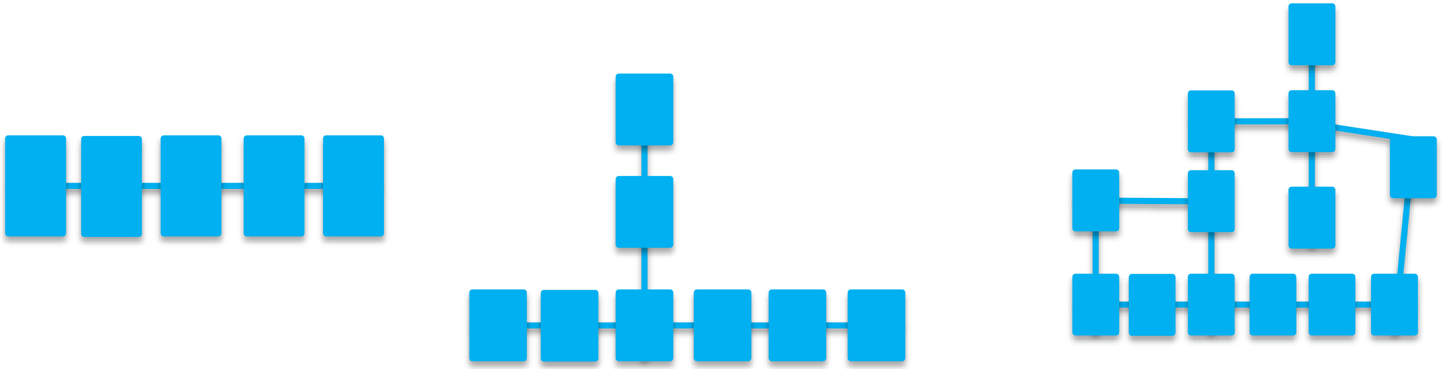


Amylopectin forms semicrystalline "particles"



Topology

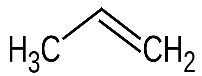
- Polymers can be **linear**, **branched**, and **cross-linked**
- Dictated by the chemistry of the **monomer** (functionality) and the "**polymerization**" process
- Functionality of <u>two</u> gives linear polymers*

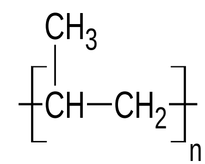


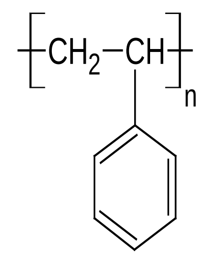
Morphology

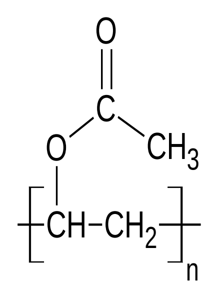
- Polymer **morphology** is the 2-D/3-D form of the polymer chains when aggregated together
- Certain polymers can be ordered (at least parts) and show **symmetry**, as found in crystals (symmetric arrangement of atoms around a plane)
  - Semi-crystalline morphology of a polymer contains regions that are **amorphous** and regions that are **crystalline**

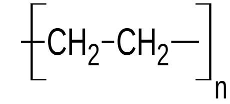
Turning small molecules into polymers

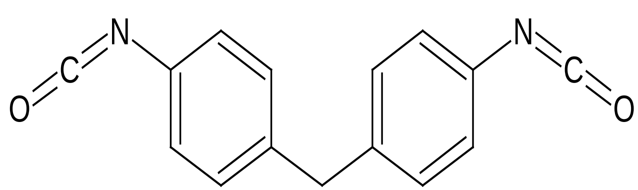
- Free radical polymerization 
  - Radical based addition reactions
  - Three step process
- Step growth polymerization
  - Reaction between functional groups











Create macromolecules by joining many small molecules together (**polymerization**)

- Small molecule (M) → "monomer"

M M M M M M M M

M M M M M M M M

- Macromolecule = "polymer"

M-M-M-M-M-M-M-M-M-M-M-M-M-M

Polymerization pathways: Chain polymerization

M= molecules that form covalent bonds, while propagating reactive species (*)

I* Initiating reactive species

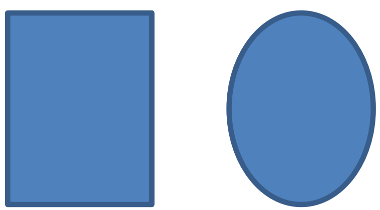
M M M M M M M Monomers

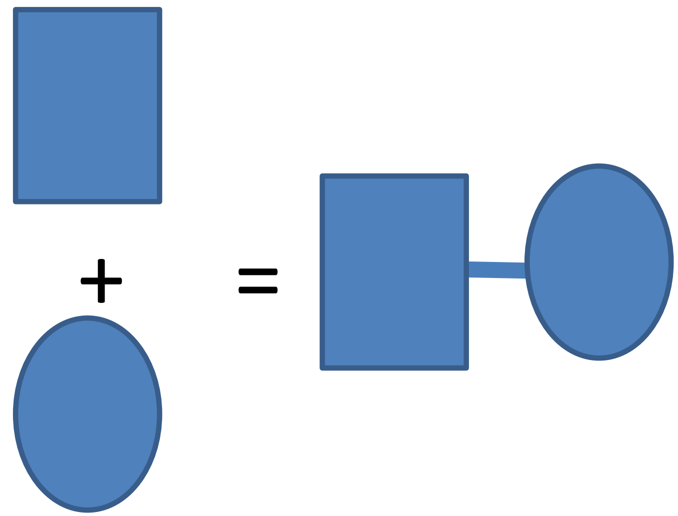
1. initiate $\mathbf{I^* + M \rightarrow I\text{-}M^*}$

2. propagate $\mathbf{I\text{-}M^* + M \rightarrow I\text{-}M\text{-}M^*}$

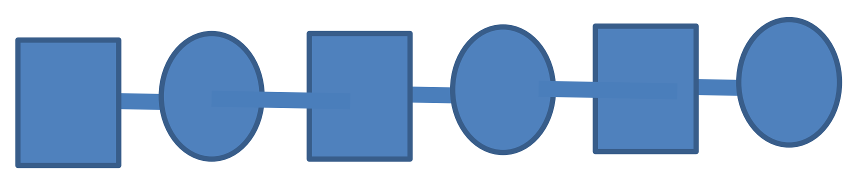
3. terminate $\mathbf{I\text{-}M\text{-}[M]_n\text{-}M}$

Polymerization pathways: Step growth





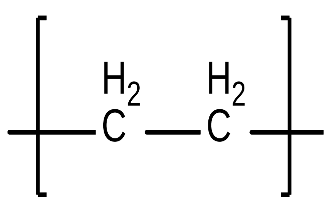
Monomer A and
B with reactive
functional
groups



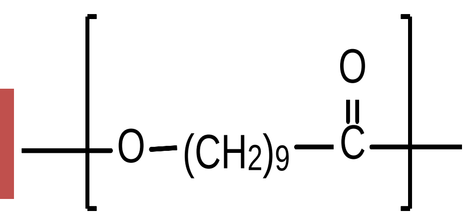
Repeat units

- When monomers are formed into polymers, the monomers form a repeat unit
  - For **addition/free radical** reactions, the number of monomers that get linked together along a chain is equal to the the degree of polymerization (DP)
  - For **condensation/step growth** reactions either two monomers come together to form a repeat unit or two difunctional monomers come together to form two repeat units

$H_2C{=}CH_2$

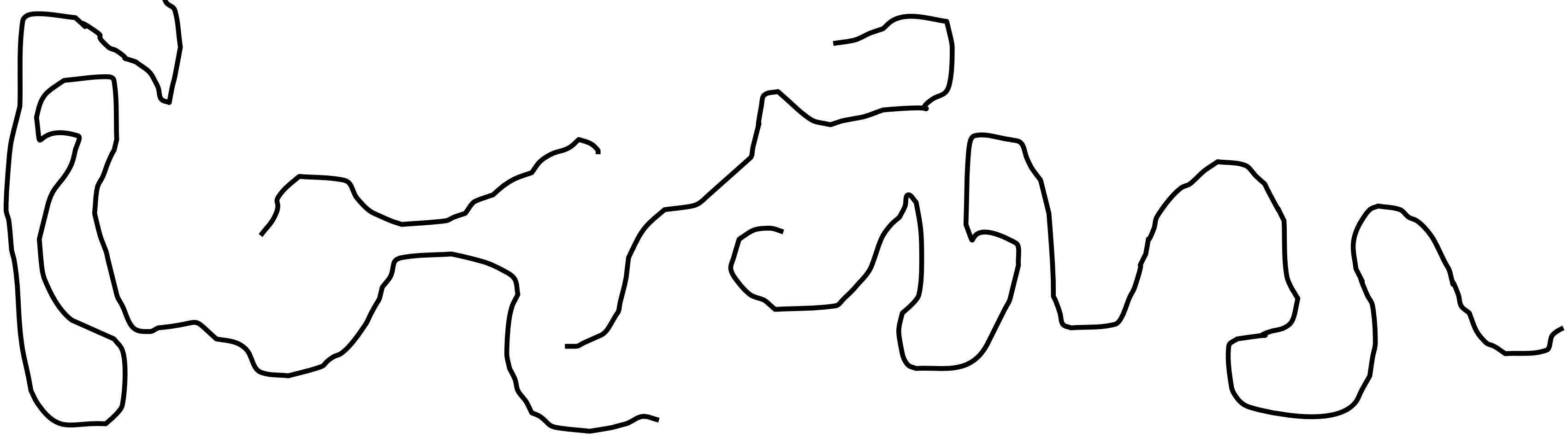


$HO(CH_2)_9CO_2H$



Molecular weight (MW)

- Polymerization causes formation of many, many chains.
- Distribution of sizes because inability to make a uniform MW from a random process
- There is a molecular weight distribution (Bell curve)
  - Or there is a given frequency of chain length from very small chains to very large chains



Molecular weight

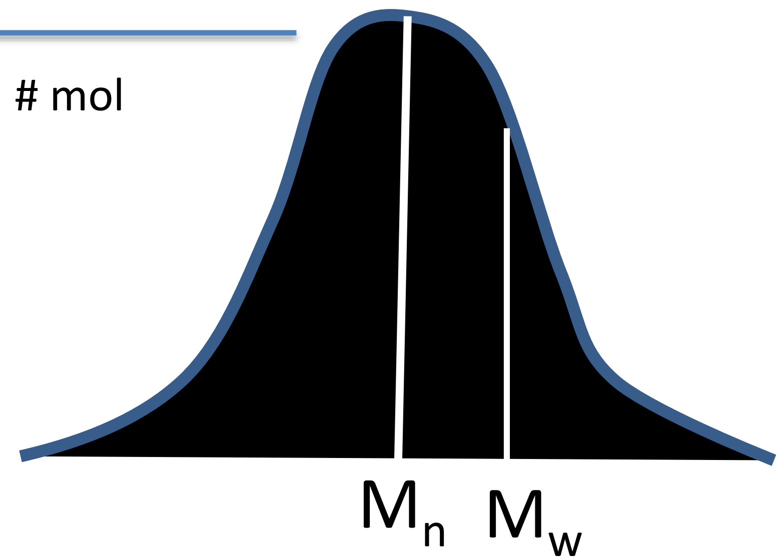
- Moments of the molecular weight distribution
  - Number average
    - The number of molecules of each weight in the sample are counted
  - Weight average
    - The weight fraction of each species times its molecular weight
  - Z average
    - Higher molecular weight order average, impacts melt processing
- Polydispersity index (PDI)
  - Ratio of the weight average MW over the number average MW

Molecular weight calculations

$$\overline{M_n} = \frac{\sum N_i M_i}{\sum N_i}$$

mol x g/mol + # mol x g/mol +…

Total # mol



$$\overline{M_w} = \frac{\sum N_i M_i^2}{\sum N_i M_i}$$

mol x (g/mol)^2 + # mol x (g/mol)^2 +…

mol x g/mol + # mol x g/mol +…