Topic 1

The Macromolecule

1.1 The Macromolecule

- Pat Doyle begins; he will teach the next three lectures.

    - They've broken the class up into modules taught alternatingly.
    - Aside: Alfredo has taught this course 10 times; Doyle never has (he's replacing Greg Rutledge this year).

- Announcements.

    - Slides and homework 1 have been posted.
    - Slides should be posted before lecture, but may not be posted much before.

- Lecture outline.

    - Connectivity: Thermodynamic limit, architecture, and molecular weight.
    - Configurations: Structural, chemical, stereo, and geometrical isomerism.
    - Conformations: Rotational isomeric states.

- **Connectivity**: The joining of small parts (monomers) into larger molecules (polymers).

- **Degree of polymerization**: The number of repeat units in a polymer. *Denoted by N*.

    - Derivable from the molecular weight(s).

- Example: Polyethylene.

    - In this course, vinyl examples will be our workhorses, but we will "riff off of them" to other polymer types.
    - The **repeat unit** here is CH_2CH_2, consistent with the IUPAC nomenclature of poly*ethylene*.
    - Ethylene is also the monomer.
    - The end groups do look different, but the **thermodynamic limit** addresses them.

- **Repeat unit**: A part of a polymer whose repetition would produce the complete polymer chain (except for the end groups) by linking the repeat units together successively along a chain.

- **Thermodynamic limit**: The finding that as $N \to \infty$, the end group chemistry matters less. *Also known as* **polymer limit**.

    - The thermodynamic limit is also sometimes discussed in the context of statistical mechanics, where collective behavior also matters more than individual or picoscale.

- **Glass transition temperature**: The temperature at which a substance will go from brittle to kind of rubbery. *Denoted by* $T_{\mathbf{g}}$.

- **Flory-Fox correlation**: The simple model that the T_g of a polymer asymptotically approaches a limit $T_\mathrm{g}(M \to \infty)$ for higher and higher molecular weights at some empirically derived rate A. *Given by*

$$T_\mathrm{g}(M_\mathrm{n}) := T_\mathrm{g}(M \to \infty) - \frac{A}{M_\mathrm{n}}$$

  – Alkane series often obey this simple $1/x$ relation.

- Another example of thermodynamic limits: Regardless of polymer structure, a power law defines polymer viscosity.
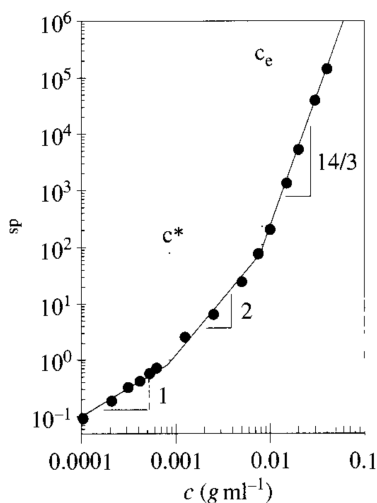

Figure 1.1: Polymer viscosity scales universally by power laws.

  – Namely, polymer viscosity increases up to a critical concentration c^* at a slpe of 1, then to an entanglement concentration c_e at a slope of 2, and then at a slope of 14/3 past that.
  – Thus, there are three universal scaling regimes.
  – A log-log plot is used to show power-law scalings, like in high school trigonometry!
  – Aside: Power laws are present everywhere once you get big enough, down to the volume of our lungs relative to our bodies in bigger and bigger animals.

- This class isn't super stringent on nomenclature, but it's good to know terms for when we read papers (Table 1.1).

  – Alfredo will talk about block copolymers a good bit!

- Polymer architectures.

  – Linear polymers.
    - Polyrotoxanes and other supramolecular assemblies can have interesting properties. Example: Catenated DNA!
  – Cross-linked systems (nice gelation).
  – Branched polymers can have a single monomer, or multiple as in graft (Table 1.1).
  – Dendritic polymers have different generations with regular branching for very dense structures.
  – There are a few more classes, as well.

Copolymer type	Arrangement of monomeric units	Representation	Connective	Example
unspecified	unknown or unspecified	(A-*co*-B)	*-co-*	poly[styrene-*co*-(methyl methacrylate)]
statistical	obeys known statistical laws	(A-*stat*-B-*stat*-C)	*-stat-*	poly(styrene-*stat*-acrylonitrile-*stat*-butadiene)
random	obeys Bernoullian statistics	(A-*ran*-B)	*-ran-*	poly[ethene-*ran*-(vinyl acetate)]
alternating	alternating	(AB)$_n$	*-alt-*	poly[(ethylene glycol)^a-*alt*-(terephthalic acid)]
periodic	periodic with respect to at least three monomeric units	(ABC)$_n$ (ABB)$_n$ (AABB)$_n$ (ABAC)$_n$	*-per-*	poly[formaldehyde-*per*-(ethene oxide)-*per*-(ethene oxide)]
block	linear arrangement of blocks	–AAAAA–BBBBB–	*-block-*	polystyrene-*block*-polybutadiene
graft	polymeric side chain different from main chain^b	–AAAAAAAAAAA– $\|$ B B B B B $\|$	*-graft-*	polybutadiene-*graft*-polystyrene

^{a} ethane-1,2-diol, ^{b} main chain (backbone) is specified first in the name.

Table 1.1: IUPAC nomenclature of copolymers.

- We'll now discuss some nomenclature on molecular weight.

- Aside: Other than nature, synthetic chemists cannot make dispersity 1 polymers; "polymer chemists aren't gods, despite some thinking they are."

- **i-mer**: A segment of a polymer with degree of polymeriation i.

- **M_i**: The molecular weight of the i-mer. *Given by*

$$M_i := iM_0$$

- **M_0**: The molecular weight of the repeat unit in a polymer chain.

- **n_i**: The number of i-mers.

- **Number fraction** (of an i-mer): The probability of picking an i-mer out of solution when picking a chain. *Denoted by x_i. Given by*

$$x_i := \frac{n_i}{\sum_i n_i}$$

- **Weight fraction** (of an i-mer): The probability that a repeat unit picked out of solution belongs to an i-mer. *Also known as* **weight fraction**. *Denoted by w_i. Given by*

$$w_i := \frac{n_i M_i}{\sum_i n_i M_i} = \frac{n_i(iM_0)}{\sum_i n_i(iM_0)} = \frac{in_i}{\sum_i in_i}$$

  - Note that in_i is the total number of monomers in the i-mer, and $\sum_i in_i$ is the total number of monomers in solution.

- **Number-average molecular weight**: The arithmetic mean of the molecular masses of the individual macromolecules. *Denoted by M_n. Given by*

$$M_\mathrm{n} := \sum_i x_i M_i = M_0 \cdot \frac{\sum_i in_i}{\sum_i n_i}$$

- **Weight average molecular weight**: A mesurement of molecular weight that gives more contribution to higher-weight molecules. *Denoted by* $\boldsymbol{M_{\mathbf{w}}}$. *Given by*

$$M_{\mathrm{w}} := \sum_i w_i M_i = M_0 \cdot \frac{\sum_i i^2 n_i}{\sum_i i n_i}$$

- Both M_{n} and M_{w} look like moments of a distribution (i.e., first and second moment).

  – We could generalize even more, but we don't need to.

  – However, to figure out if we have a tight or wide distribution, we often look at ratios of our moments. This leads to the following definition.

- **Dispersity**: A measure of the breadth of the distribution of fragment molecular weights in a polymer sample. *Also known as* **polydispersity index**, **PDI**. *Denoted by* **Đ**. *Given by*

$$Đ := \frac{M_w}{M_n} = \frac{\text{second moment}}{\text{first moment}}$$

- In Lodge and Hiemenz (2020), they also derive the **variance**. You don't need to worry about the math, though.

- **Variance**: Another measure of the breadth of the distribution of fragment molecular weights. *Denoted by* $\boldsymbol{\sigma^2}$. *Given by*

$$\sigma^2 := M_n^2 [Đ - 1]$$

- **Schultz-Zimm distribution**: An idealized mathematical model for polymer molecular weight distribution.

- With these definitions, we can now do homework problem number 1!

- Experimental techniques to measure molecular weight.

  – Size exclusion chromatography.

  – Osmotic pressure.

  – End group analysis.

  – Light scattering techniques.

    ■ More sensitive to higher moments.

- We now move onto polymer configurations.

- **Configurations**: The way things are connected or bonded together.

  – Physicists and chemists have many competing definitions of "configurations," but the one above is what we'll use in this class. Essentially, think of it as a synonym for constitutional isomerism.

  – Under this definition, you have to *break bonds* to create a new configuration.

  – We are *not* yet talking about rotamers (what we'll call **conformations**). As you make your polymers longer and longer, the conformational space you can explore gets bigger.

- There are 3 main types of structural isomers (i.e., configurations): **Positional**, **stereo**, and **geometric** isomers.

- **Positional** (isomers): Changing connectivity.

- **Stereoisomers**: Related to chiral centers.

- **Geometric** (isomers): Related to double bonds.

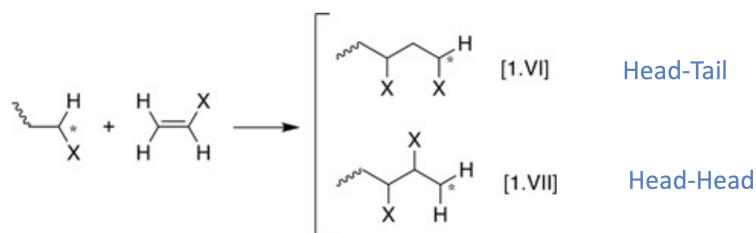- More on positional isomers.

Figure 1.2: Head-head and head-tail monomer addition.

  - **Head-head** vs. **head-tail** bonding in vinyl monomers.
  - Head-tail is more common, and differences can change the T_{g} substantially.

- **Head-head** (orientation): Monomer addition wherein the substituted carbon attaches to the growing chain end. *Also known as* **head-to-head**.

- **Head-tail** (orientation): Monomer addition wherein the *un*substituted carbon attaches to the growing chain end. *Also known as* **head-to-tail**.

- More on stereoisomers.

- Doyle reviews **chirality**, **rectus** vs. **sinister**, and the **Cahn-Ingold-Prelog nomenclature**.

- **Pseudochiral** (center): A chiral center where two of the substituents are identical *except* for chirality.

  - In this case, CIP nomenclature gives priority to the branch with more R chiral centers.

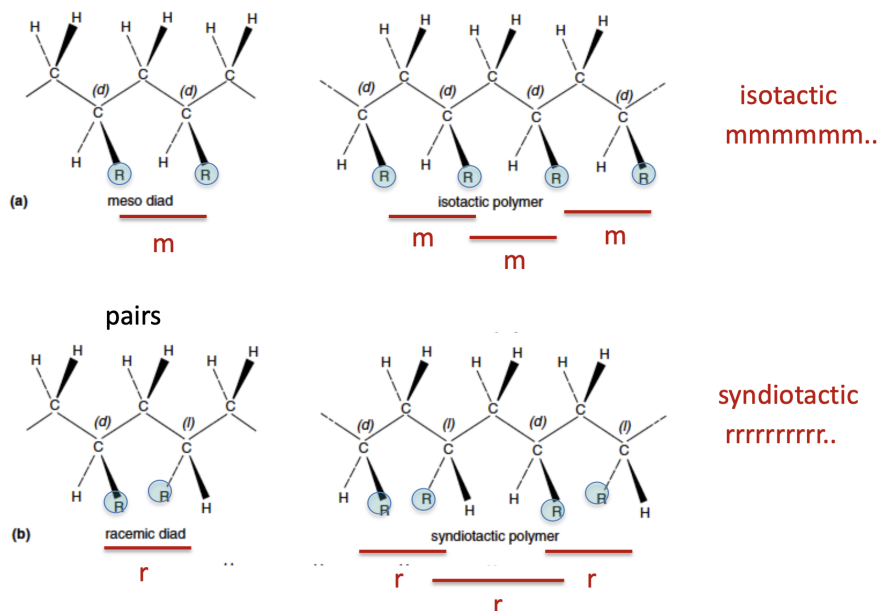- Chiral centers in polymers give rise to **tacticity**.

Figure 1.3: Tacticity.

  - There are **meso diads** and **racemic diads**; which ones you have determine if the polymer is **isotactic**, **syndiotactic**, or **atactic**.

- **Meso** (diad): Two adjacent chiral centers with a local plane of symmetry halfway between them.

- **Racemic** (diad): Two adjacent chiral centers with*out* a local plane of symmetry halfway between them.

- **Isotactic** (polymer): A polymer containing only meso diads.

- **Syndiotactic** (polymer): A polymer containing only racemic diads.

- **Atactic** (polymer): A polymer containing both meso and racemic diads.

- Example: Atactic polystyrene tends to be more amorphous than syndiotactic or isotactic polymers, which can be semicrystalline.

  – Nobel prize (1963) to Ziegler and Natta for a catalyst generating isotactic polystyrene (PS-it).

    ▪ Note that the initial Ziegler-Natta catalysts weren't metallocenes! The introduction of these types only came later.

  – Syndiotactic polystyrene (PS-st) came later in 1986 and had superior properties.

    ▪ PS-st crystallizes an order of magnitude faster than PS-it; has half the entanglement molecular weight; and is commonly used today in auto parts, electronics, and medical equipment.

- Tacticity is often measured by certain splittings (or their absence) in ^{1}H NMR.

  – Isotactic polymers put the geminal methylene protons into distinct chemical environments; syndiotactic polymers do not. Atactic polymers will have a mix of both, and the mix can be quantified with integration.

  – ^{13}C NMR can be used, too.

- More on geometric isomers.

  – Example: Polybutadiene can be formed *trans* or *cis*, as guided by a catalyst.

  – Natural rubber is *cis*-1,4-polyisoprene. Other types of tree sap can give *trans*-1,4-polyisoprene.

- We now move onto polymer conformations.

- **Conformations**: The spacial arrangements possible (or "probable," taking energy into account) for a polymer.

  – No bonds are *broken* here, just rotated.

- Reviews **Newman projections**.

  – **Staggered** configuration is defined as $0°$.

  – **Eclipsed** configuration then starts at $60°$.

  – There are energy pentalties to being in different conformations.

    ▪ As one example, eclipsed is higher energy than staggered due to sterics.

    ▪ Generally sinusoidal relation in a plot of potential energy V against dihedral angle θ.

    ▪ The energy difference between rotamers is approximately $3k_\mathrm{B}T$, which is not huge but big enough that the system will spend most of its time in the valleys. Each "valley" is a **conformer**.

    ▪ So then since probability is proportional to $\mathrm{e}^{-V/k_\mathrm{B}T}$, the probability that a molecule will be staggered is greater than that it will be eclipsed.

  – In molecules longer than ethane, we break degeneracy of the valleys.

  – The rapid growth of conformers: Ethane has 3 conformers. Propane has 3^2. Butane has 3^3. Decane has 3^10. Polyethylene with $N = 10^5$ already has on the order of $10^{47\,000}$ possible conformers, a huge conformational space.

- ■ This is because each bond has 3 valleys!
- ■ Many of the models we'll develop are ways of enumerating these conformations in relation to some higher-order measurement of the polymer, such as the **n-band difference**.
- ■ Polymers are indeed often moderately sized coils rather than fully stretched out rods.
- ■ Example: 166 kbp DNA (approximately 684 **Kuhn steps**, discussed next lecture) can be videotaped moving around, and it never fully elongates.
- ■ Stretched out polymers shrink back over some characteristic time.
    - – Polymers with high degrees of polymerization result in many possible conformations without breaking bonds — this is what we'll discuss in the next two lectures!

- A good converions to keep in mind: $2.5\,\mathrm{kJ/mol} \approx 1k_{\mathrm{B}}T$.

- Today is probably the most jampacked bits and pieces day; other lectures will be more focused, but this is important background.