

Topic 1

The Macromolecule

1.1 The Macromolecule

9/9:

- 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 polyethylene.
 - 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 $N \rightarrow \infty$, 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_g .*
- **Flory-Fox correlation:** The simple model that the T_g of a polymer asymptotically approaches a limit $T_g(M \rightarrow \infty)$ for higher and higher molecular weights at some empirically derived rate A . *Given by*

$$T_g(M_n) := T_g(M \rightarrow \infty) - \frac{A}{M_n}$$

- Alkane series often obey this simple $1/x$ relation.
- Another example of thermodynamic limits: Regardless of polymer structure, a power law defines polymer viscosity.

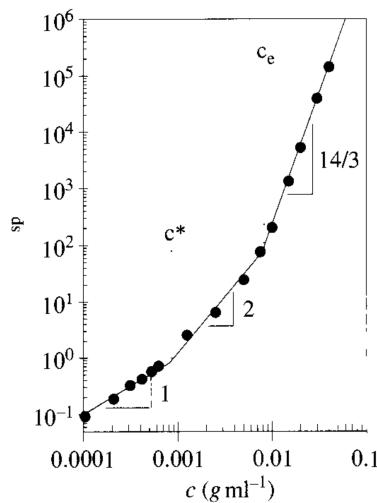


Figure 1.1: Polymer viscosity scales universally by power laws.

- Namely, polymer viscosity increases up to a critical concentration c^* at a slope 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.
 - Polyrotaxanes 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- <i>co</i> -B)	- <i>co</i> -	poly[styrene- <i>co</i> -(methyl methacrylate)]
statistical	obeys known statistical laws	(A- <i>stat</i> -B- <i>stat</i> -C)	- <i>stat</i> -	poly(styrene- <i>stat</i> -acrylonitrile- <i>stat</i> -butadiene)
random	obeys Bernoullian statistics	(A- <i>ran</i> -B)	- <i>ran</i> -	poly[ethene- <i>ran</i> -(vinyl acetate)]
alternating	alternating	(AB) _n	- <i>alt</i> -	poly[(ethylene glycol) ^a - <i>alt</i> -(terephthalic acid)]
periodic	periodic with respect to at least three monomeric units	(ABC) _n (ABB) _n (AABB) _n (ABAC) _n	- <i>per</i> -	poly[formaldehyde- <i>per</i> -(ethene oxide)- <i>per</i> -(ethene oxide)]
block	linear arrangement of blocks	-AAAAA-BBBBB-	- <i>block</i> -	polystyrene- <i>block</i> -polybutadiene
graft	polymeric side chain different from main chain ^b	-AAAAAAAAAA- B B B B B 	- <i>graft</i> -	polybutadiene- <i>graft</i> -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*

$$M_i := i M_0$$

- ***M₀*:** 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*

$$w_i := \frac{n_i M_i}{\sum_i n_i M_i} = \frac{n_i (i M_0)}{\sum_i n_i (i M_0)} = \frac{i n_i}{\sum_i i n_i}$$

- Note that *i n_i* is the total number of monomers in the *i*-mer, and $\sum_i i n_i$ 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*

$$M_n := \sum_i x_i M_i = M_0 \cdot \frac{\sum_i i n_i}{\sum_i n_i}$$

- **Weight average molecular weight:** A measurement of molecular weight that gives more contribution to higher-weight molecules. *Denoted by M_w . Given by*

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

- 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 D . Given by*

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

- 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 σ^2 . Given by*

$$\sigma^2 := M_n^2[D - 1]$$

- **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.

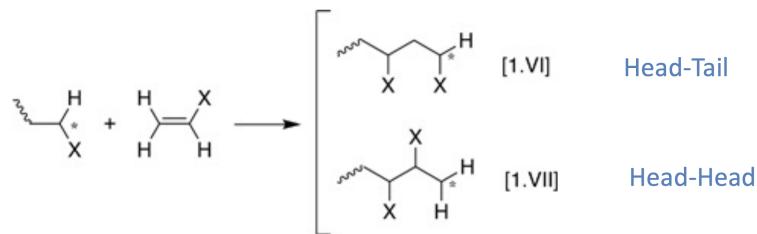


Figure 1.2: Head-head and head-tail monomer addition.

- **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 unsubstituted 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**.

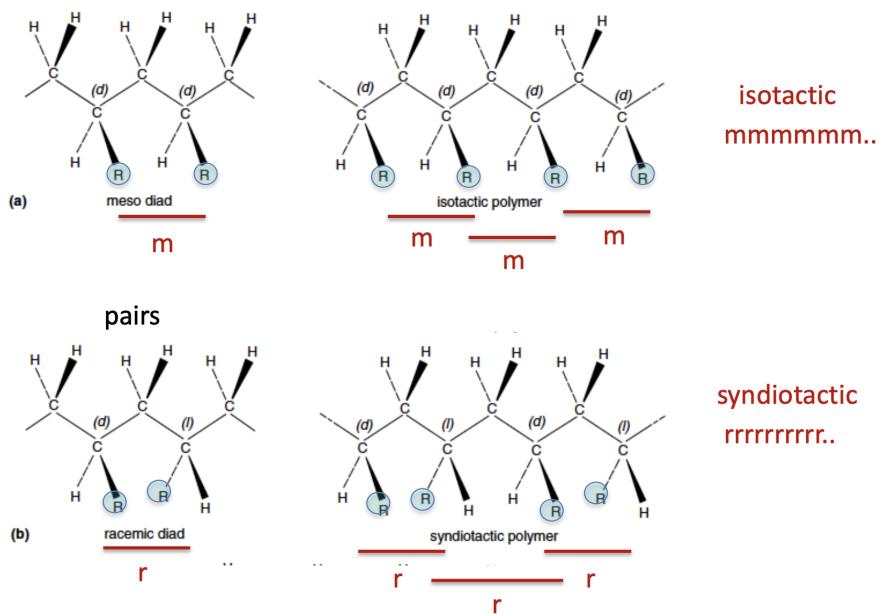


Figure 1.3: Tacticity.

- 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 *without* 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 ^1H 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 penalties 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 $3k_{\text{B}}T$, 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 $e^{-V/k_{\text{B}}T}$, 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^{47000} 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 conversions to keep in mind: $2.5 \text{ kJ/mol} \approx 1k_B T$.
- Today is probably the most jampacked bits and pieces day; other lectures will be more focused, but this is important background.

1.2 Conformation: Ideal Chains

9/11:

- Lecture outline.
 - Conformation (degrees of freedom).
 - Ideal chain models.
 - Entropic elasticity.
- Many material properties we care about are correlated with the size of the polymer.
- This size is measured by a vector \mathbf{R} that goes from one end of the polymer to the other.

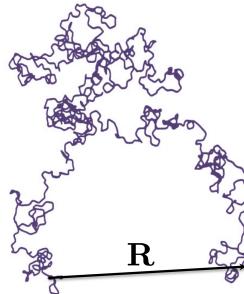


Figure 1.4: End-to-end polymer vector.

- We define \mathbf{R} as the sum of all constituent bond vectors \mathbf{l} (end-to-end of each chemical bond along the backbone). Symbolically,

$$\mathbf{R} := \sum_{i=1}^n \mathbf{l}_i$$

- Note that \mathbf{R} has length $|\mathbf{R}| = R$.
- Today, we will look at several models that can be used to calculate the expected length of this vector, $\langle R \rangle$.

- Freely Jointed Chain (FJC) model.

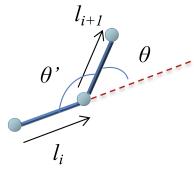


Figure 1.5: A joint in a polymer chain.

- In this model, there are no restrictions on how adjacent bonds rotate relative to each other. Rather, this is just a random walk. In effect, this means that there are no energy barriers and no excluded volume.
 - It follows that $\langle R \rangle = 0$.
- However, while $\langle R \rangle = 0$, we have

$$\begin{aligned} \langle R^2 \rangle &= \left\langle \sum_{i=1}^n \mathbf{l}_i \cdot \sum_{j=1}^n \mathbf{l}_j \right\rangle \\ &= \sum_{i=1}^n \sum_{j=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= \sum_{i=1}^n \langle \mathbf{l}_i \cdot \mathbf{l}_i \rangle + \sum_{i=1}^n \sum_{j=1, j \neq i}^n \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= nl^2 + 0 \end{aligned}$$

- The second term goes to zero as $n \rightarrow \infty$ because there is no correlation among segments (i.e., they are randomly oriented).
- This gives us the following important scaling law.

$$\langle R^2 \rangle^{1/2} \propto n^{1/2}$$

- This means that scaling is consistent with the polymer taking a “coil-like” conformation.
- This combined with the fact that the polymer’s fully stretched length is nl gives us the following expression for the number of backbone bonds in a polymer.

$$\frac{(\text{fully stretched length})^2}{\langle R^2 \rangle} = n$$

- Note that Lodge and Hiemenz (2020) uses θ for the *complement* of bond angle, as in Figure 1.5. Other texts may use a different convention.
- Now, let’s refine the FJC by accounting for nearest neighbor correlations.
- First, we’ll look at a polymer with only two segments (i.e., $n = 2$)
 - Suppose every joint is *fixed* at complementary angle θ , but there is no energy penalty to rotate in ϕ .
 - From Figure 1.5, trigonometry tells us that

$$\mathbf{l}_i \cdot \mathbf{l}_{i+1} = l^2 \cos \theta$$

- Thus, under the conditions of this model,

$$\begin{aligned}\langle R^2 \rangle &= 2l^2 + \sum_{i=1}^2 \sum_{\substack{j=1 \\ j \neq i}}^2 \langle \mathbf{l}_i \cdot \mathbf{l}_j \rangle \\ &= 2l^2 + 2 \langle l^2 \cos \theta \rangle \\ &= nl^2(1 + \cos \theta)\end{aligned}$$

- The important takeaway is that with this chemical realism, the chain is bigger than in the previous model!

■ It is also noteworthy that the nl^2 scaling relation is retained.

- This is a precursor to the freely rotating chain, where we can rotate in ϕ but not in θ .

- Let's now look at the full Freely Rotating Chain (FRC) model.

- As we elongate the chain, there is a slow decay of “memory of correlation” since ϕ rotates freely. Eventually (see Lodge and Hiemenz (2020, pp. 239–40) for the derivation), we asymptote to

$$\langle R^2 \rangle = nl^2 \underbrace{\left(\frac{1 + \cos \theta}{1 - \cos \theta} \right)}_{C_n}$$

where C_n may be an empirically derived **characteristic ratio**.

- Model 3: Symmetric hindered rotations.

- Recall from last class that certain rotational conformations have lower energies than others.
- As such, we can give a Boltzman weighting to the energetic valleys.
- Thus, we reevaluate our hindered rotations with a Boltzmann weighting and the following expression crashes out of the math.

$$\langle R^2 \rangle = nl^2 \underbrace{\left(\frac{1 + \cos \theta}{1 - \cos \theta} \right) \left(\frac{1 + \langle \cos \phi \rangle}{1 - \langle \cos \phi \rangle} \right)}_{C_\infty}$$

■ Note that it's still just nl^2 times a constant!

- The **characteristic ratio** C_∞ can be calculated for models or obtained from experiments. The following rearranged definition is also important.

$$C_\infty := \frac{\langle R^2 \rangle_0}{nl^2}$$

- Alert: Be aware of sign changes due to different conventions for θ and ϕ in different texts!

- There are tables of characteristic ratios in both Lodge and Hiemenz (2020) and Rubinstein and Colby (2003).

Polymer	Structure	C_∞
1,4-Polyisoprene (PI)	$-(\text{CH}_2\text{CH}=\text{CHCH}(\text{CH}_3))-$	4.7
1,4-Polybutadiene (PB)	$-(\text{CH}_2\text{CH}=\text{CHCH}_2)-$	5.5
Polypropylene (PP)	$-(\text{CH}_2\text{CH}_2(\text{CH}_3))-$	6.0
Poly(ethylene oxide) (PEO)	$-(\text{CH}_2\text{CH}_2\text{O})-$	6.7
Poly(dimethyl siloxane) (PDMS)	$-(\text{OSi}(\text{CH}_3)_2)-$	6.8
Polyethylene (PE)	$-(\text{CH}_2\text{CH}_2)-$	7.4
Poly(methyl methacrylate) (PMMA)	$-(\text{CH}_2\text{C}(\text{CH}_3)(\text{COOC}\text{H}_3))-$	8.2
Atactic polystyrene (PS)	$-(\text{CH}_2\text{CHC}_6\text{H}_5)-$	9.5

Table 1.2: C_∞ values for common polymers at 413 K.

- C_∞ gets bigger with bigger side chains.
- Typical range is 5-10; can go up to 20 or higher, though.
- Example: What is the size of a polyethylene molecule at 413 K and having molecular weight 10^4 g/mol?
 - Approach: We want to find $\langle R^2 \rangle$ and take its square root; that will be our answer.
 - We can look up that the length l of a typical C–C bond is 0.154 nm.
 - Based on the molecular weight and the known weight of the ethylene (CH_2CH_2) repeat unit,

$$N = \frac{10^4 \text{ g/mol}}{28 \text{ g/mol}} \approx 357.1$$

- Because there are two carbon-carbon bonds per repeat unit, $n = 2N$.
- Thus,

$$\begin{aligned} \langle R \rangle &= \langle R^2 \rangle^{1/2} \\ &= [nl^2 C_\infty]^{1/2} \\ &= [(2 \cdot 357.1)(0.154 \text{ nm})^2(7.4)]^{1/2} \\ \langle R \rangle &\approx 11 \text{ nm} \end{aligned}$$

- Let's compare the answer in the above example to the straight chain estimation.

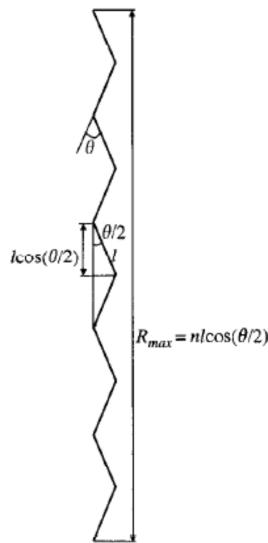


Figure 1.6: Straight chain estimation of a polyolefin.

- In this case,

$$R_{\max} = nl \cos(\theta/2)$$

- We can look up that for a typical C–C bond, $\theta = 180^\circ - 109.5^\circ = 70.5^\circ$.
- Thus,

$$\begin{aligned} R_{\max} &= nl \cos(\theta/2) \\ &= (2 \cdot 357.1)(0.154 \text{ nm}) \cos(70.5/2) \\ R_{\max} &\approx 90 \text{ nm} \end{aligned}$$

- This calculation is a bit tedious, so Kuhn refined the coarse grained FJC model to be computationally simpler.
- Model 4: Kuhn's Equivalent Chain.

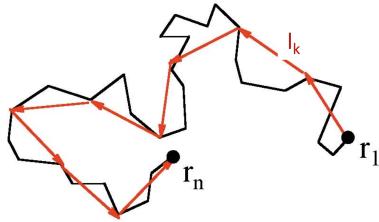


Figure 1.7: Kuhn steps.

- Building off of models 3 and 1, let's postulate the existence of an FJC along our polymer. This FJC will have N steps of length l_k , where l_k is a Kuhn step.
- This gives us two variables to define. We thus need two equations by which to define them.

- Equation 1: By the universal scaling law,

$$Nl_k^2 = \langle R^2 \rangle = C_\infty n l^2$$

- Equation 2: If the total length of the chain is R_{\max} , and the chain is being broken up into N Kuhn steps each of length l_k , then

$$R_{\max} = Nl_k$$

- By solving this system of equations, we can then define N and l_k purely in terms of previously derived variables.

- **Kuhn step:** A subsegment of a polymer chain with length defined as follows. *Denoted by l_k . Given by*

$$l_k := \frac{\langle R^2 \rangle}{R_{\max}} = \frac{C_\infty n l^2}{R_{\max}}$$

- **Number of Kuhn steps:** The number of Kuhn steps in a polymer chain. *Denoted by N . Given by*

$$N := \frac{R_{\max}}{l_k} = \frac{R_{\max}^2}{C_\infty n l^2}$$

- Example: In the case of a fully elongated carbon-carbon chain (Figure 1.6), the number of Kuhn steps is

$$l_k = \frac{C_\infty n l^2}{R_{\max}} = \frac{C_\infty n l^2}{n l \cos(\theta/2)} = \frac{C_\infty l}{\cos(\theta/2)}$$

- Note that the symbols R_{\max} and L will be used interchangeably for the straight-chain length of a polymer.
- R_{\max} largely depends on the chemistry of the polymer (e.g., specific atoms' bond angles).
- We'll now look at some models for "stiff" chains, such as dsDNA or microtubules.
 - These tend to have even higher C_∞ values.
 - Note that twists in the chain are *much* bigger than individual nucleobases.
 - Molecular simulations of 75 bp dsDNA shows barely any bending. Indeed, there is a high correlation between end vectors even though they are very far away.

- A model for very stiff polymers: The Worm-Like Chain (WLC).

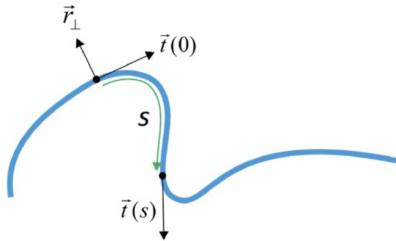


Figure 1.8: Worm-like chain.

- Represent a segment as an infinitesimal elastic rod.
- This rod has a contour you can be some point s along, where $s \in [0, L]$.
- The direction of the rod is defined by a tangent vector $\mathbf{t}(s)$.
- We also give the rod some bending energy U_b , related to how the tangent changes as we go along s . But physically, this is just curvature squared. To get the right units, we throw in a bending stiffness parameter κ_b , which incorporates some chemical / molecular details. Throw in a $1/2$ from mechanics definitions, and we get

$$U_b = \frac{1}{2} \kappa_b \int_0^L \left(\frac{\partial \mathbf{t}}{\partial s} \right)^2 ds$$

- An implication of this is that correlation decays exponentially per

$$\langle \mathbf{t}(0) \cdot \mathbf{t}(s) \rangle = e^{-sk_B T/\kappa_b}$$

- I.e., you use memory of how oriented you are in one part of the chain when you get farther away from that point.
- Since $\kappa_b/k_B T$ has units of length by dimensional analysis, we can define it to be the **persistence length**.
- From this tangent correlation function, we can calculate many interesting properties — including the mean squared end-to-end distance!

$$\langle R^2 \rangle = 2aL \left[1 - \frac{a}{L} \left(1 - e^{-L/a} \right) \right]$$

- The calculation is complicated, so Dolye skips it.
- This equation reveals some interesting polymer behavior in two limits: That of *long* and *short* stiff polymers.
 - When the polymer gets long, $a/L \rightarrow 0$ and $\langle R^2 \rangle \rightarrow 2aL$.
 - When the polymer gets short, $a/L \rightarrow \infty$ and $\langle R^2 \rangle \rightarrow L^2$.
 - This makes intuitive sense as if it's short, it should be roughly straight and have end-to-end distance approximately equal to its length!
 - Note that in real life, there *are* polymers where the persistence length is longer than the length of the polymer! These behave like rigid rods.
- Lastly, it follows from definition of Kuhn steps that

$$2aL = \langle R^2 \rangle = Nl_k^2 = \frac{R_{\max}}{l_k} \cdot l_k^2 = Ll_k$$

- Thus, the Kuhn length is twice the persistence length! Symbolically,

$$2a = L$$

- **Persistence length:** A characteristic length over which a stiff polymer loses memory of its orientation along other parts of the chain. *Denoted by a . Given by*

$$a := \frac{\kappa_b}{k_B T}$$

- In conclusion, two biggest models to remember: Kuhn model (rigid steps) and WLC (continuum approximation with persistence length for semi-rigid chains).
- Example: Actin has a persistence length of $10\text{ }\mu\text{m}$; since most cells are smaller than this, actin is functionally a rigid rod within a cellular context.
- Example: Measuring persistence length of dsDNA.
 - Adsorb DNA onto a surface that loosely binds it, so that it can still move around but won't fall off.
 - Then look at 1000s of strands next to each other and calculate tangent lengths!
 - Reference: Kundukad et al. (2014).
- Example: Bottlebrush polymers in cartilage.
 - These have highly charged side chains, but fewer with age.
 - This causes more bending.
 - We can observe this with atomic force microscopy.
- Example: As you increase the concentration of salt in solution, you shrink the **Debye length** and also the persistence length.
 - This modifies the effect of charges on dsDNA.
- Example: Actin cytoskeleton filaments.
 - Made out of polymerized protein subunits.
 - A very thin polymer, biologically speaking.
 - Very long persistence length, as mentioned earlier.
 - As cells move, they push actin against the cell membrane to distort it! This works because actin is a very rigid rod, so rigid that it can overcome the membrane pressure.
- Example: Conjugated polymers.
 - They calculated the persistence length using DFT, and then measured it experimentally.
 - Some of their polymers are stiffer than dsDNA!
 - Rotation around one particular engineered bond is used to estimate persistence length.
- **Flexible** (polymer): A polymer for which chain length is much greater than persistence length.
- **Semi-flexible** (polymer): A polymer for which chain length is approximately equal to persistence length.
- **Rod-like** (polymer): A polymer for which chain length is much shorter than persistence length.
- Summary of ideal chains.
 - All chains show a similar, universal scaling relation that $R \approx N^{1/2}$.
 - For ideal chains, local interactions set the rigidity length scale and excluded volume is not significant.
 - This approximation is ok for dilute solutions at **theta conditions** and polymer **melts**.

- **Theta condition:** When you've essentially turned off excluded volume for the chain.
- **Polymer melt:** A condition in which the polymer is essentially in a solution of itself.
- Nomenclature for polymer solution regimes.

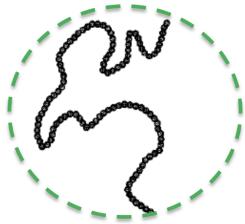


Figure 1.9: The volume occupied by polymers.

- **Hard volume** (of a polymer): The volume occupied by the chain, where each repeat unit is considered to occupy a sphere with radius equal to the bond length and the polymer is the sum of these “beads” touching each other. *Denoted by v . Given by*

$$v \propto nl^3$$

- The volume of each bead is thus on the order of the bond length.
- **Pervaded volume** (of a polymer): The sphere encapsulating the volume in which the polymer chain is *expected* to move around. *Denoted by V . Given by*

$$V \propto \langle \mathbf{R}^2 \rangle^{3/2} \propto n^{3/2} l^3$$

- From this, we can see that

$$\frac{v}{V} \propto n^{-1/2}$$

- It follows that the pervaded volume is mostly empty as n becomes large.
- **Critical concentration:** The concentration at which all polymers in solution can “see” each other. *Denoted by c^* .*

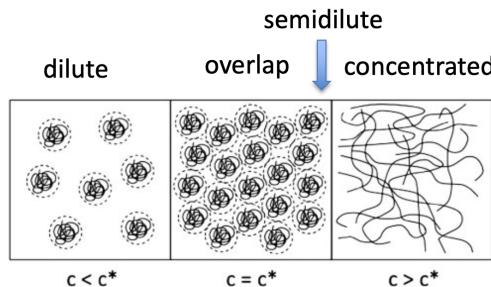


Figure 1.10: Concentration regimes.

- In dilute solutions, polymers will all be coiled up within their own pervaded volume and will not interact.
- When they reach the critical concentration, all of the pervaded volumes are essentially touching each other.

- Past the critical concentration, we get entanglement and no longer see individual polymer coils in their own pervaded volume.
- This is the same c^* as in Figure 1.1!
- Unifying implication: These concentrations are related to pervaded volume, which is related to expected size.
- Next time.
 - Adding in excluded volume, which will wrap up our discussion on chains.
 - Then Alfredo on thermodynamics of interactions.

1.3 Chapter 1: Introduction to Chain Molecules

From Lodge and Hiemenz (2020).

9/14:

- Begins with the uses and history of polymers.
- **Macromolecule:** A large or long molecule.
- **Polymer:** A macromolecule made by repeating one (or a few) chemical units many times.
 - All polymers are macromolecules, but not all macromolecules are polymers.
- Lodge and Hiemenz (2020) will often write molecular weights without the unit “g/mol,” but we should write them with this unit.
- Some types of polymerization involve only the joining of monomers; others involve this joining, but with the elimination of a small molecule byproduct (like H_2O or HCl).
- Figure 1.6’s derivation uses the **law of cosines** from high school trigonometry.
- Polyolefin size: Based on typical C–C bond angles and lengths...
 - The straight-chain length is approximately $N \cdot 0.25 \text{ nm}$;
 - The actual end-to-end distance is approximately $N^{1/2} \cdot 0.25 \text{ nm}$.
- **Oligomer:** A molecule made of repeat units but for which $N < 10$.
- Note that *polymers* typically have $M \geq 1000 \text{ g/mol}$, but this cutoff is arbitrary (and probably on the low side).
- Polymer architectures.
- **Branched** (polymer): A linear molecule with additional polymeric chains issuing from its (linear) backbone.
- **Short-chain branch:** A small substituent (such as a methyl or phenyl group) on the repeat unit.
 - These are generally not considered branches.
- Branching can occur *by design, adventitiously, or through grafting*.
 - By design, we may introduce polyfunctional junctions into the formulation.
 - Adventitiously, “an atom [may be] abstracted from the original linear molecule, with chain growth occurring from the resulting active site” (Lodge & Hiemenz, 2020, p. 7).
 - This commonly happens with polyethylene!
- **Graft to** (polymerization): Pre-formed but still reactive polymer chains can be added to sites along an existing backbone.

- **Graft from** (polymerization): Multiple initiation sites along a chain can be exposed to monomer.
 - Note: **Graft through** polymerization is not covered.
 - For simple branching (no loops), a molecule with v branches has $v + 2$ chain ends.
 - **Comb** (polymer): A polymer in which a series of relatively uniform branches emanate from along the length of a common backbone.
 - **Star** (polymer): A polymer in which all branches radiate from a central junction.
 - **Cross-linked** (polymer): A polymer with such extensive branching that the macroscopic object may be considered to consist of essentially one molecule.
 - These polymers are given cohesiveness by covalent bonds instead of intermolecular forces, and thus have very different properties from non-cross-linked polymers.
 - **Hyperbranched** (polymer): A polymer that is highly branched, but in which the components remain as discrete entities.
 - **Dendrimer**: A class of hyperbranched polymers that are tree-like, in that they have completely regular structures formed by successive condensation of branched monomers.
 - Start with a B_3 junction (generation 0), condense on three AB'_2 monomers and deprotect (generation 1), condense on six AB'_2 monomers and deprotect (generation 2), etc.
 - At generation 6 or 7, the surface of the molecule becomes so congested that adding further complete generations is impossible.
 - **Cycle** (polymer): A polymer in which the two chain ends react to close the loop. *Also known as ring.*
 - **Homopolymer**: A polymer with only a single kind of repeat unit.
 - Note that polymers made with two different monomers can still be homopolymers. For example, a polyester condensed from diacid and diol *monomers* still only has one kind of *repeat unit*.
 - **Copolymer**: A polymer with two kinds of repeat units.
 - **Terpolymer**: A polymer with three kinds of repeat units.
 - **Multicomponent** (polymer): A polymer with four or more kinds of repeat units.
 - **Random** (copolymer): A copolymer in which the A-B sequence is governed strictly by chance, subject only to the relative abundances of repeat units.
 - **Statistical** (copolymer): A copolymer in which monomer addition at a growing chain end may depend on the preceding monomer(s), according to a statistical law.^[1]
 - **Alternating** (copolymer): A copolymer containing a regular pattern of alternating repeat units.
 - **Block** (copolymer): A copolymer containing long, uninterrupted sequences of each monomer.
 - **n -block** (copolymer): A block copolymer containing n uninterrupted sequences of each monomer.
 - For small n , the terms **diblock**, **triblock**, and **tetrablock** are commonly used.
 - If a triblock copolymer consists of a sequence of monomer A, followed by monomer B, followed by monomer A, we may call it an **ABA triblock copolymer**.
- 9/16: • In addition to classifying polymers by architecture, we can classify them by the reactions used to make them.

¹The copolymers we make with CCs are all statistical, since addition is governed by probability-based reactivity ratios.

- **Addition** and **condensation** polymerization are the most common, but there are more.
- **Addition** (polymerization): A polymerization for which the following three statements apply. *Also known as chain-growth. Defined by*
 1. The repeat unit in the polymer and monomer have the same composition (although bonding is different in each).
 2. The polymerization proceeds through a **chain reaction** mechanism, with either free radicals or ionic groups responsible for propagating the chain reaction.
 3. The product molecules *often* have an all C–C backbone, with pendant substituent groups.
- **Condensation** (polymerization): A polymerization for which the following three statements apply. *Also known as step-growth. Defined by*
 1. The polymer repeat unit arises from the reaction of two different functional groups, which *usually* originate on different monomers. In this case, the repeat unit is different from either monomer. In addition, small molecules are *often* eliminated during the condensation reaction.
 2. Mechanistically, the reactions occur in steps; in other words, the formation of the linkage functional group between two small molecules is not essentially different from that between one of these growing polymers and a monomer.
 3. The product molecules have the functional groups formed by the condensation reactions interspersed regularly along the backbone of the polymer molecule.
- Properties of condensation polymerizations.
 - Either two difunctional monomers with different functional groups, or one difunctional monomer with a functional group of each kind.
 - Beware the creation of loops!
 - Very sensitive to impurities.
 - Example: Trace methanol in a polyester condensation could cap some carbonyl derivatives as methyl esters, preventing them from reacting further.
 - Functionality greater than 2 can introduce branching.
 - Introduction of reagents with varying functionalities in carefully controlled amounts affords control over polymer size and geometry.
- The physics in this text apply equally well to organic and inorganic (e.g., PDMS) polymers.
- Biopolymers are briefly introduced.
- Polymer nomenclature.
- IUPAC recommendation.
 - Polymers formed from a single monomer.
 - Take the IUPAC name of the monomer, enclose it in parentheses, and add the prefix “poly”.
 - Example: poly(1-chloroethylene) for PVC.
 - Polymers need not be synthesized from the monomer named. For example, poly(1-hydroxyethylene) is synthesized from the hydrolysis of poly(1-acetoxyethylene).
 - Polymers formed from multiple monomers.
 - Apply the preceding rules to the repeat unit.
 - Example: poly(hexamethylene adipamide) is nylon-6,6.
 - Commercially important cross-linked polymers.
 - Typically go without names, or at best, by specifying the monomers that go into it.

- Example: “Phenol-formaldehyde resin” for bakelite.
- Notes on common names.
 - Many polymers have a common/outdated chemical name, a trade name, and/or an acronym.
 - Examples: polyethylene glycol, Teflon, PVC.
- On positional isomerism.
 - Head-to-head addition is more common (1) at higher temperatures and (2) with halogenated monomers.
 - Head-to-tail is dominant because of (1) resonance stabilization at the head positoin and (2) steric exposure of the tail.
 - Polymer cleavage can provide information about head-head vs. head-tail polymerization: Since diols are cleavable by periodate, poly(vinyl alcohol) can have its weight measured, be subject to cleavage conditions, and have the resultant fragments' weight remeasured to calculate the average frequency of diols.
- Stereoisomerism reviewed.
- On geometric isomerism.
 - Not only can you have *cis*- or *trans*-backbones, but isoprene (for example) can polymerize through either — or both! — of its double bonds.