

CHEM 39100 (Polymer Synthesis) Notes

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Week 1

???

1.1 ???

- 1/4:
- Announcements.
 - TA: Max Weires (mweires@uchicago.edu).
 - Talks slowly enough.
 - This first lectures is a catchall to get everyone set.
 - This course is cross-listed MENG 25110/35110 and CHEM 39100.
 - There are handouts on Canvas. Ask to be added!
 - HW will be given out by Max; it's not graded, but it's critically important that (a) we do it and (b) we understand it. Exam questions are very much like the HW.
 - 1 HW question will appear in the Midterm and Final, so if we know the HW well, free marks!
 - Scheduled discussion section at 11:30?? Max will schedule a second one.
 - The entire grade is based on the two exams.
 - Feel free to interrupt him if needed.
 - Rowan's contact info.
 - hi
 - Use a good book
 - Odian's book is much more detailed than we need, but it's a great reference.
 - The Stevens book is a better introductory book if this is our first brush with the subject.
 - Ask him to publish the slides before lecture.
 - Schedule. *table*
 - Two online classes while Rowan is traveling.
 - Midterm: 2/1.
 - Final: During finals week.
 - Point of this class: I give you a polymer structure, and you tell me how to make it.
 - Example polymers.
 - Polycarbonate.
 - Poly...
 - Kevlar

- PVC.
- PP.
- By the end of this class, we should be able to make all of these.
- What do we need to consider when making a polymer?
 - Polymer size: The physical properties of a polymer change with its size.
 - Hugely important; don't let anyone tell you otherwise.
 - Polymer synthesis means nothing unless you can (a) measure its MW and (b) control it.
 - Polydispersity or dispersity (PD or “D stroke”, IUPAC preferred): PDI - Polydispersity index.
 - Polymers *always* have a distribution of MWs.
 - Chemistry of the polymers.
 - What atoms are in it; determines synthesis.
 - General structure: Linear, branched, star, etc.
 - Are there potential isomers (think copolymers; proteins are copolymers with 20 amino acids!).
 - Control of sequence in copolymers: Random, Block, etc.
 - What are the chain ends?
 - Can they help us do more chemistry? If they're well-defined, they may be useful; varied, less so.
 - Rate of reaction (can it be controlled).
 - Is this done very quickly, or does it take 20 days.
- The above considerations are questions that should be asked of any polymer synthesis...
- Note: The objective of the course is to understand the variety of tools that chemists have at their disposal to synthesize polymers.
- **Polymer molecules:** Formed by the reaction of many monomer molecules, which add to each other. The resulting chain molecules exhibit new properties.
- Effect of molecular weight in polyethylene. *table*
 - Molecular weights in the millions can stop a bullet.
 - Implication: The chemical structure is no longer enough to tell you all properties.
- How do we define the molecular weight? Degree of polymerization and MW. *picture; polymer parts*
 - The physical properties change with the length of chains.
 - Averages are used, since a polymer material consists of many chain molecules of different length.
 - **Structural unit** = **monomer unit** = residue of monomers A,B... incorporated in the polymer chain.
 - **Repeating unit** = segment of one or more structural units.
 - PCL given as an example!
 - What people get wrong on the exam: Bracket placement. Be very careful about identifying the repeating unit!!
 - In the left case, $DP = n$, but in the right case, $DP = 2n$.
- **Number-average degree of polymerization:** The average number of structural units per polymer chain. Denoted by $\overline{X_n}$, \overline{DP} .
 - The overbar means “average.”

- Polymer size or chain length.
 - The physical properties of a polymer change with its size.
 - So, we need to know the polymer size or molecular weight.
 - Two most important:
 - **Number average molecular weight**

$$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x}$$

- Total weight of molecules divided by total number of molecules.

- **Weight average molecular weight**

$$\overline{M}_w = \frac{\sum W_x M_x}{\sum W_x} = \frac{\sum N_x M_x^2}{\sum N_x M_x}$$

- Total weight of molecules divided by total weight of molecules??

- **Degree of polymerization**

$$\overline{X}_n = \frac{\overline{M}_n}{M_{\text{repeat unit}}}$$

- We do it two different ways because some experimental techniques give us \overline{M}_n , some give us \overline{M}_w , and some give us both.

- **Carothers Equation**

$$\overline{X}_n = \frac{1}{1-p}$$

where p is the extent of the reaction (or fraction of conversion).

- We'll come back to this equation over and over again.

- Measuring average molecular weights.

- Techniques which measure properties that depend on the number of molecules give M_n .
 - End group analysis (e.g., with NMR).
 - Osmometry.
- Techniques which measure properties that depend on the size or mass of the molecules give M_w .
 - Light Scattering.
- Other techniques are relative, i.e., properties compared to known standards.
 - Gel electrophoresis.
 - ...

- Dispersity. *table*

- In synthetic polymers, the individual chain molecules are not the same weight.
- A measure of the breadth of distribution of the molecular weights in a polymer is the dispersity (used to be termed the PDI):

$$D = \frac{\overline{M}_w}{\overline{M}_n} > 1$$

- Hypothetical single MWt polymer has $D = 1.000$. Could be made with a tedious 20-step synthesis, but Rowan doesn't recommend that.
- We'll talk a bit about living polymerizations.
- Radical often gives 2, but can be 1.5.

- Addition and step-growth (we'll talk more about them in a minute) give 2.0.
 - The chemistry has to be almost quantitative (99.9% if we wanna use it). At 90%, we're already at PDI of 10.
 - Technical term: Shitty polymers, which are basically just oils that do nothing to us.
 - Almost all reactions have side reactions that kill termination.
- High-conversion polymers have things dying often and the PDI grows.
- The chemistry: The two fundamental mechanisms for polymerization.
 - **Chain-growth:** Addition polymerization. E.g., Olefins, some ring openings.
 - **Step-growth:** Condensation polymerization. E.g., polyesters, polyamides.
 - Not perfect correspondence, though: Polyurethanes use step-growth, not condensation for some reason.
$$\text{OCN-R-NCO} + \text{HO-R}'\text{-OH} \longrightarrow \text{Polyurethane}$$
 - Why distinguish between chain-growth and step-growth?
 - The mechanisms and setups are quite different.
- Chain (addition) polymerizations. *picture*
 - $\text{R}^* + \text{Monomer} \longrightarrow \text{R-M}^*$
 - And then repeat.
 - So a few initiations and a lot of polymers lead to fast buildup of molecular weight.
 - Only monomer, polymer, and a small number of growing chains present at any one time.
 - This is key!
 - New car smell: We're getting high on the monomer, which wasn't fully removed from the polymers; the monomers are more volatile, hence us smelling it!
 - We have monomer at any stage of reaction, except we go to 100% completion, but this almost never happens because of viscosity increasing.
 - All that happens as we go through time is we get more polymer chains; MW doesn't really vary throughout the process.
- Step-growth polymerization. *picture*
 - Any two components can add together to increase molecular weight.
 - Slow buildup of MW.
 - High conversions required to get high MW.
 - This is doable, but it takes some skill.
 - Much easier to do chain growth.
 - If we made a car with step-growth, no new car smell! Monomer disappears very quickly.
- Comparisons of chain- and step-growth polymerizations.
 - This has been a favorite question in the past.
- Double-bond polymerizations.
 - This is really the focus of the first half of the course.
 - Driving force for the reaction is the conversion of 1 π -bond (ca. 585 kJ/mol to 2 σ -bonds (2x ca. 330 kJ/mol)).
 - The overall polymerization generally involves 4 basic reactions: Initiation, propagation, termination, and chain transfer.

Step	
Growth by the reaction of any two oligomers	Growth by addition of monomer
Rapid loss of monomer species (First reaction produces dimer)	Some monomer remains
Driving force for the reaction is removal of the condensation product	Driving force for this reaction energetics, i.e., conversion
Molar mass increases slowly throughout	Molar mass of backbone
Ends remain active	Chain not active
...	

Table 1.1: Comparison of chain- and step-growth polymerizations.

- **Initiation:**
- **Termination:** *Also known as death.*
- **Chain transfer:** New reactive species formed at same time growing polymer chain is deactivated (terminated).
- Next few slides are for the engineers: There are only 3-4 OChem-era reaction mechanisms, which we'll go over right now; chem majors can yawn.
 - Most reactions involve an electron-rich molecule (**nucleophile**) and an electron-poor molecule (electrophile).
 - Rowan “is VERY PICKY with curved arrow formalism.”
 - Radical reactions involve the coupling of two unpaired electrons, or can attack a double bond.
 - A lot of polymerization involves radical chemistry.
 - A reactive carbon center (R^*) can exist as a electrophile (carbenium ion, carboncation), carbon radical, or nucleophile (carbanion).
 - Only electron-poor double bonds will react with the anion. Only nucleophilic double bonds will react with carbocations.
 - Implication: Not every double bond can be polymerized the same way!
 - The reactive species can be a free radical (neutral reactive species [RS]), cationic (RS is positive and electrophilic), and anionic [reactive species is negative and nucleophilic].
 - So a common question is, given a certain kind of bond, what kind of initiator would you use?
 - The reactive species depends on the substituents on the molecule.
 - A bit of electron withdrawing often helps polymerization.
 - Radical: Requires X,Y to be EWG (to stabilize the radical).
 - Cationic: Requires X,Y to be EDGs (to stabilize the electron-poor carbenium ion).
 - Anionic: Requires X,Y to be EWGs (to stabilize the electron-rich carbanion).
- Some monomers and how they can be polymerized. *table*
- How to tell if a substituent is EDG or EWG.
 - Electron density from the O lone pairs donate into the π -bond. Other heteroatoms with a lone pair can also donate electrons in this manner. Alkyl groups can also “donate” electron density to the double bond, but it is much weaker.
 - EWGs: Electron density from the π -bond is withdrawn by the carbonyl into the ester. Most substituents that have a multiple bond adjacent to the double bond will withdraw electrons, e.g., CN. Halides are also EWGs.
 - Key point: Any time you can delocalize electron density, that makes the system more stable.
 - If you can share electron density across many atoms, that dramatically increases stability.

- Styrene derivatives; The effect of resonance.
 - “If you look at it the wrong way, styrene will polymerize.”
 - It’s very reactive and can follow any of the mechanisms: Radical, cations, and anions can all be shared among 4 carbons!
 - It’s not magic why certain initiators work; it’s chemistry!
 - “Last thing you want to do is spend a month of your PhD trying to make a polymer only to realize you used the wrong initiating system.”
- Insertion “coordination” polymerization.
 - In this type of polymerization, the metal is coordinated to the chain end.
 - It also coordinates to the monomer, in the process of activating it, before inserting the monomer between the chain end and metal.
 - Ziegler-Natta and ...
 - We’ll have a class on these.
- Ring-opening polymerizations (ROP).
 - Thermodynamic driving force here is the release of ring strain.
 - This is how polyethylene oxide is made.
 - ROP usually requires an initiator, c.f., vinyl addition polymerizations.
 - ROP can be initiated by either anionic or cationic polymerizations depending on the monomer.
 - Polymerization, generally, by addition of monomer only to reactive chain end, c.f., vinyl addition polymerizations.
- Living polymerizations.
 - Chain polymerizations where chain transfer and termination are either very small or nonexistent and all chains are initiated at once.
 - Generally step-growth (Rowan knows no chain-growth examples).
 - There’s no chain death here; without death, the system is *living*!
 - Normal chain growth: With time, number of polymer chains increases and \overline{M}_n stays the same.
 - Living growth: Same number of polymer chains, but \overline{M}_n increases.
 - Living polymerizations are a great way to control molecular weight! If you want a certain MW, just stop after a certain amount of time.
 - Kinetics: $R_t = 0$; no termination. $R_i \gg R_p$: Rate of initiation must be faster than rate of propagation so that all chains start growing at once and they all increase MW at the same time.
 - If we have these two kinetic conditions, then

$$X_n = \frac{[M]_{\text{consumed}}}{[I]}$$

and $D \approx 1$.

- Step-growth polymerization.
 - Esterification.
 - Acid chloride plus alcohol makes ester and HCl.
 - This is condensation.
 - Polyesterification.

- Just take a di-acid chloride and a diol and condense!
- HCl isn't a great nucleophile, but it can still reverse the polymerization.
- Thus, to get high MW, you want to withdraw the condensation product.
- Types of polymers formed by step-growth polymerizations. *picture with 6 subfigures*
 - Technically, “polyimine” should be “polyamine,” but whatever says Rowan.
- General mechanisms: Substitution reactions.
 - SN2, two molecules involved in the RDS.
 - SN1, one molecule involved in the RDS.
- General mechanism: acyl substitution.
 - Polyester or polyamide formation.
 - Remember the famous/infamous tetrahedral intermediate!
 - Rate depends on how good the LG is; chloride is a great leaving group, which is why acid chlorides are so reactive!
 - Note.
 - This is a substitution reaction; however, the mechanism is slightly different from a normal SN2 mechanism.
 - The electrophile can be an acid chloride, acid anhydride, ester, or just an acid, although the reaction is slower the worse the leaving group X is.
 - Acids need like 200 °C.
- Comparison of chain- and step-growth polymerizations.
 - Chain-growth: Slow initiation, fast propagation yields increasing number of chains with same weight.
 - $p = R_p / (R_p + R_t + R_{ct})$ from the Carothers Equation, where R_p is rate of propagation, R_t is rate of termination, and R_{ct} is rate of chain transfer.
 - Step-growth: Exponential increase in weight toward the end; needs high conversion! Essentially, weight follows the equation 2^n : Monomers to dimers to tetramers to octomers to 16-mers, on and on.
 - p is percent of functional groups reacted divided by 100.
- Possible isomers in polymers.
 - Structural isomers.
 - Sequence isomers.
 - Stereoisomers.
 - Geometric isomers.
 - Regioisomers.
- **Structural isomers.**
 - Linear vs. branched.
 - Branched polymers have very different physical properties to linear polymers; less crystalline...
- Sequence isomerism.
 - There are generally two possible ways in which a monomer can add to a reactive site.

- Most olefinic monomers give almost exclusively HD polymers, mainly on account of steric hindrance and stability of the active site.
- However, some polymers (e.g, PVF) have a significant amount of HH and TT placements.
- ?? could be the weakest link in our polymers.
- Stereoisomers.
 - Stereochemistry of addition polymerization of olefins.
 - The two faces of a double bond or reactive center – prochirality.
 - So for any polymerization of an unsymmetrical double bond, there are another two possible ways for the monomer to be added to the polymer chain.
- Tacticity.
 - Stereoisomerism plays a major role in controlling the polymer's ability to crystallize.
 - Three general types: Isotactic, syndiotactic, atactic.
 - Remember by drawing letters I,S through the polymer shape!
- Dyad tacticity is defined to be the fraction of pairs of adjacent units that are either isotactic or syndiotactic to one another.
 - Triads exist, too!
- Random tacticity.
- Radical polymerization.
 - When we do a polymerization, we'll generally...

Week 2

???

2.1 ???

1/9:

- Finishing up from last time's lecture to start.
- Regio- and geometric isomers.
 - Some monomers can react at two different sites (e.g., 1,4-butadiene).
 - There's also *cis* and *trans* isomerism when double bonds are in the polymer.
 - Three types of potential isomers.
 - Structural isomers: 1,2- or 1,4-addition; this depends on the regiochemistry of the polymerization.
 - ...
- **Copolymer**: A polymer in which two or more different monomers are incorporated into the polymer chain.
 - **Terpolymers** and **tetrapolymers**, as well.
 - **Statistical/random** vs. **alternating** copolymers.
- **Terpolymer**: A copolymer with 3 different monomer repeat units.
- **Tetrapolymer**: A copolymer with 4 different monomer repeat units.
- **Statistical** (copolymer): A copolymer in which the comonomers appear in irregular, unspecified sequences along the chain. *Also known as random.*
- **Alternating** (copolymer): A copolymer in which the comonomers occur in alternation.
- **Block** (copolymer): A copolymer in which a long, linear sequences of polymer A is joined to a long, linear sequence of polymer B.
- **Graft** (copolymer): ...
- Polymer end groups.
 - For a linear polymer, there are two end groups.
 - The more branches, the more end groups.
 - End group chemistry is often important and allows us to do fun stuff.
 - For addition and some ROPs, one end group comes from the initiator and the other from the termination process.

- “If we know how it dies, maybe we can keep it from dying a bit longer. A little bit of autopsy on the polymer allows us to keep it alive and growing for longer”
 - For step-growth polymers, the end groups are determined by the monomer.
 - Knowledge of the structure of the end groups allows. . .
 - Determination of molecular weight (up to about 30,000 because after that, they’re just too small to characterize).
 - Synthesis of block copolymers.
- Key points of lecture 1, in summary.
 - Many definitions related to macromolecules.
 - Different macromolecular...
 - Main takeaways:
 - Mainly definitions.
 - If you understand the definitions, it will make everything else easier!
- Reminder that this first lecture content is introducing us to stuff that we’ll see throughout the rest of the course!
- Moving onto today’s lecture!
- The next 2-3 lectures will be about radical polymerization of olefins.
 - We could easily do 10 lectures on this stuff!
 - There’s so much and so many things we can control and play with.
- We’ll be focusing on radical addition polymerization and the general propagation mechanism.
 - Works for most olefin monomers.
- **Radical polymerization:** ...
- This method produces a lot of synthetic plastics.
- Examples:
 - PE (LDPE, LLDPE, HDPE).
 - PP.
 - PVC.
 - PS.
 - Acrylates and fluoropolymers (e.g., teflon).
 - *More in the slides.*
- Olefin substituents.
 - Isobutene and vinyl ethers don’t really work, but pretty much everything else can.
 - Anything with a strong EDG won’t work.
 - This is useful to remember when he gives us a monomer and wants us to tell him how to polymerize it!
- Overview of free radical process.
 - Key: The *rate*.
 - Difficult to measure because there are a ton of different reactions at different points all happening in the same one pot.

- Initiation, propagation, termination.
 - We'll talk about each of these separately, plus their kinetics, and then pull everything back together.
- The mechanism of radical polymerization.
 - Initiation step: Throw a radical progenitor into the reaction, heat it up so that it splits into two radicals that *then* do the reaction.
 - Reaction.
$$\text{I} \xrightarrow{k_d} 2 \text{R} \cdot$$
 - k_d is given by the Arrhenius equation
$$k_d = A e^{-E_a/RT}$$
 - ...
- Thermal initiators.
- AIBN.
 - AIBN (2,2'-azobisisobutyronitrile) will be found in almost every polymer lab. *screenshot*
 - The reaction goes because N_2 is a thermodynamic sink, and because the nitrile group acts as an EWG to stabilize the radical.
 - Where do k_d and E_a come from?
 - We can measure time vs. nitrogen evolution and know that the two will have a logarithmic relationship so t vs. $\ln(l_0/l)$ will be linear.
- Benzoyl peroxide.
 - This one is even slightly stronger than AIBN.
 - The weak O–O bond is the driving force for this decomposition.
 - Same stuff as in acne creme and tooth whiteners!
- There are hundreds of examples of thermal initiators! *table*
 - Which one you uses depends.
 - For one, you want your initiator to be soluble in the monomer.
 - If the monomer boils below the initiation temperature, that's not good!
 - Oftentimes, polymer chemists get so caught up in the kinetics that they forget practical things like, "is my initiator soluble in my monomer?"
- Key takeaways on thermal initiators.
 1. The difference in the decomposition rate...
- Initiator half-lives.
 - We don't need to memorize this table, but it's good to know!
 - We should be able to look at a chemical structure and know which of two initiators initiates faster.
- Two ways to do the course: Memorize absolutely everything, or understand how to work things out.
- The fate of free radicals.
 - A small percentage of benzoyl radicals will decarboxylate and give you the phenyl radical.

- Most of the reaction will react via the middle route because the radical there can be stabilized by resonance delocalization into the aromatic ring (vs. 2) and we're not breaking aromaticity (vs. 3).
- Not all radicals initiate new chains; a big waste product is BPO, which is when two radicals react. This brings us to the next topic.
- **Initiation efficiency:** The fraction of radicals formed in the primary step of initiator decomposition which are successful in initiating polymerization. *Denoted by f . Given by*

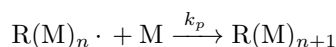
$$f = \frac{\text{radicals incorporated into the polymer}}{\text{radicals formed by the initiator}}$$

- Temperature- and solvent-dependent.
- ...
- Primary reasons $f < 1$.
 - **Solvent cages.**
 - Increasing viscosity of the reaction medium.
- Viscosity.
 - This is chain-growth, so we get HWt polymers really quickly.
 - Increasing viscosity means that the lifetime of radicals in solvent cages increases.
 - Example: AIBN for polystyrene decreases from 0.75 to 0.2 as conversion increases from 30% to 60%.
- **Solvent cage:** An ephemeral, transient group of solvent molecules that forms around radicals.
 - The presence of a solvent cage traps radicals and increases rate of recombination... basically molecules in solution act like they are encapsulated.
 - This is an explanation of why our f might be crappy, but we don't really worry about it or do anything about it.
- Mechanism and kinetics of initiation.
 - Two reactions: Decomposition and addition to monomer.
 - Decomposition is the RDS (think of the long half-lives!).
 - Typical values for $k_d = 10^{-3} \text{ s}^{-1}$...
 -
 - Thus, the rate R_i of initiation will equal the rate R_d of decomposition, yielding the differential equation

$$R_i = R_d = -2 \frac{d[I]}{dt} = \frac{d[R\cdot]}{dt} = 2k_d[I]$$
 - Taking f into account,

$$R_i = 2k_d f [I]$$
- Initiation is the easy step, and you see how much that was!
- We now move into propagation.
- Mechanism and kinetics of propagation.
 - k_{p2} is the rate of monomer to dimer.
 - k_{p3} is the rate of dimer to trimer.
 - Instead of having to consider thousands of rate constants, the rate of reaction is independent of molecular weight to a very good approximation.

- Thus, a general scheme is



- It follows that the rate of propagation is

$$R_p = k_p[\text{M}][\text{M}\cdot]$$

- Typical values for $k_p = \dots$
- The fact that the propagation kinetics work so well implies that there's no reason to do polymerizations at high temperature *except* for the issue of the initiator.

- Mechanism and kinetics of termination.

- $\text{cnc} = [\text{H}]$ command

- Several mechanisms.
- You can have termination via combination. This is k_{tc} :

$$R_{tc} = 2k_t[\text{M}\cdot]^2$$

- You can have termination via disproportionation.
- *Similar kinetics.*
- There are other forms of death (such as reacting with an initiator radical), but these two are dominant.
 - For example, the concentration of initiator is so much lower than that of growing polymers that it is much more likely for two growing polymers to mutually terminate.
- These varying forms of death imply that you don't have control over chain ends in a radical mechanism.
- Overall rate of termination:

$$R_t = 2k_2[\text{M}\cdot]^2$$

- The rate of propagation is faster than the rate of termination because the rate of propagation depends on $[\text{M}]$, which is very large (much larger than $[\text{M}\cdot]$).

- This is true even though $k_t \gg k_p$; it's just that $[\text{M}\cdot] \lll [\text{M}]$.

- ...

- Olefin substituents.

- Free radical polymerizations can be carried out with most vinyl monomers.
- Radical stabilization of the growing polymer happens with most species.
- However, there are exceptions.
 1. Strong EDGs.
 2. 1-alkyl olefins and 1,2-dialkyl olefins.
- Remember: Propylene, for example, cannot be polymerized under free radical conditions.
 - This is because of delocalization/resonance because an allyl radical is much more stable than the polymer radical.
- Reactivity. *scale*
 - Reactive monomers have substituents which stabilize the polymeric radical by resonance stabilization.
 - So styrene is one of the most reactive monomers.
 - The greater the gain in stability, the greater the incentive for the monomer to react.

- There are exceptions: We can polymerize ethylene, even though its substituents don't help; styrene will always react first with a radical.
 - It's flipped with growing radical stability, though: A radical generated in the middle of building PE will react much more quickly than a radical generated in the middle of building PS.
- Thus, overall, polymerization rate is determined by a compromise between monomer and polymer reactivity.
 - Example: Vinyl acetate goes super fast.
 - Most reactive radical and most reactive monomer go the fastest.
 - What does this mean tho?? Because won't a vinyl acetate radical immediately bind to a styrene radical and then not react with vinyl acetate again?
- Olefin substituents: Structural isomerization.
 - ...
 - Tacticity.
 - **Meso diads vs. racemic diads.**
 - Lead to the 3 tacticity types...
 - The racemic form is usually slightly preferred over the meso structure because of sterics and/or electrostatic repulsion...
- W 9:30-10:30 in the morning is a second discussion section.
- Th class will be virtual.
- 300-level class has papers, plus 25% of exam.

2.2 ???

1/11:

- More on the importance of tacticity.
 - Isotactic PP is very common; it's a durable material.
 - Atactic PP is just a goo.
 - T_m vs. T_g .
- Polymerization kinetics.
 - Last class, we derived the rates of initiation, propagation, and termination.
 - How do we look at the overall rate of reaction?
 - Propagation is the RDS, so that's what's most important!
 - Rates of initiation and termination are essentially the same; this is the **steady state approximation**.
 - This allows us to say

$$R_i = R_t \quad k_d f [I] = 2k_t [M \cdot]^2$$

$$[M \cdot] = \left(\frac{k_d f [I]}{k_t} \right)^{1/2}$$

- Substituting, we obtain

$$R_p = k_p [M] [M \cdot] = k_p [M] \left(\frac{k_d f [I]}{k_t} \right)^{1/2} = k' [M] [I]^{1/2}$$

where k' combines all constants.

- To confirm that this math is valid, let's look at some experimental data.
 - The plot of R_p vs. $[I]^{1/2}$ is linear.
 - The plot of R_p vs. $[M]$ is linear.
- Linear systems work well, but only to a point, leading to...
- Autoacceleration. *picture*
 - Deviations from the general kinetic expressions do occur. One type of deviation is referred to as the **gel effect**.
- **Gel effect**: Generally, one would expect from the standard kinetic expression that R_p would decrease with increasing time/conversion as both $[M]$ and $[I]$ decrease; however, particularly in bulk or concentrated solutions, a sharp increase in R_p is observed. *Also known as Tommsdorff effect, Norris-Smith effect, Norris-Tommsdorff effect.*
 - This happens because of chain entanglements, which reduce the mobility of the polymer chain radicals.
 - Chain entanglement, like wet spaghetti, dramatically increase viscosity.
 - In such viscous media, the diffusion rates of the polymer become very low and k_t is dramatically reduced. Thus, from the equation above, an increase in both R_p and X_n occurs.
 - Recall that all termination steps require two polymer chains to come together! If they're diffusing more slowly, they're less likely to come together.
- The above allows us to think about kinetics at the molecular level.
- Other types of initiators: Redox.
 - Many redox reactions can be used to generate radicals which initiate polymerization.
 - Advantage A: Radical production occurs at a reasonable rate over a broad range of temperatures.
 - Consequence: Lower temperatures are accessible (0-50 °C) than with thermal homolysis of initiators.
 - Peroxides in combination with a reducing agent are frequently employed.
 - Hydrogen peroxide + ferrous ion: $H_2O_2 + Fe^{2+} \longrightarrow HO^- + HO\cdot + Fe^{3+}$.
 - ...
 - ...
 - Other reductants can be employed instead of Fe^{2+} ; it depends on the system!
 - Solubility can be an issue for these redox systems; these are mostly used in *aqueous* or emulsion systems.
 - If you're thinking of doing a redox polymerization, there are some changes to the rate...
- Redox initiation.
 - Return to the equation

$$R_p = k_p[M] \left(\frac{R_i}{2k_t} \right)^{1/2}$$
 - For redox initiation, we have

$$R_i = k_d[\text{reductant}][\text{oxidant}]$$
 - Thus, the polymerization rate R_p of a free radical polymerization initiated by a redox reaction is...
 - Note that in this type of initiation, only *one* radical is produced, not two!

- Other types of initiators: Photochemical.
 - Photochemical initiation¹.
 - Light absorption by some compound in the system either...
 - Directly causes the compound to decompose into radicals;
 - Leads to an excited species which transfers its energy to a second compound, which in turn decomposes into radicals.
 - Advantages.
 - Polymerization can be carried out in a spatially directed manner by irradiating selective zones: ...
- **Photochemical initiation:** When radicals are produced by irradiation of the reaction system with UV or visible light.
- Photochemical initiators.
 - Typically UV curable.
 - Consider solubility, absorption spectrum, **quantum yield**, etc.
 - Type 1: **Cleavage**.
 - 2,2-dimethoxy-2-phenylacetophenone is a super common one.
 - So is benzoin.
 - Type 2: **Abstraction**.
- **Quantum yield:** How well does the compound absorb photons going into the system?
- **Cleavage:** Unimolecular bond cleavage upon irradiation.
- **Abstraction:** Bimolecular mechanism where excited molecule reacts with a second molecule (coinitiator) to generate free radicals, e.g., benzophenone amine.
- **Kinetic chain length:** The number of monomer molecules consumed per active species (radical) which initiates a chain. *Denoted by ν . Given by*

$$\nu = \frac{R_p}{R_i} = \frac{R_p}{R_t} = \frac{k_p[M][M\cdot]}{2k_t[M\cdot]^2} = \frac{k_p[M]}{2k_t[M\cdot]} = \frac{k_p^2[M]^2}{2k_tR_p} = \frac{k_p[M]}{2(k_tfk_d[I])^{1/2}} = k''[M][I]^{-1/2}$$
 - How big the polymer is going to get.
 - The kinetic chain length is very related to the degree of polymerization.
 - Tells you what you can control to get heavier polymers!
 - Note: An increase in the rate of polymerization by increasing the radical concentration will decrease the kinetic chain length.
- **Number-average degree of polymerization:** The average number of repeat units contained in a macromolecule. *Denoted by \bar{X}_n .*
 - Related to the ν .
 - If the termination process is by combination, then \bar{X}_n .
 - If the termination process is by disproportionation, then $\bar{X}_n = \nu$.
 - If a is the fraction of chains which terminate by combination, then $\bar{X}_n = 2\nu/(2-a)$.
 - Most polymer radicals appear to terminate predominantly by coupling (almost exclusively: styrene, methyl acrylate, acrylonitrile).

¹Like in the Lin lab!

- Disproportionation increases when the propagating radical is sterically hindered or features many β -hydrogens available for transfer (methyl methacrylate undergoes termination by combination 33% with 67% disproportionation at 25 °C).

- **Number-average molecular weight:** The following quantity. Denoted by \overline{M}_n . Given by

$$\overline{M}_n = M_0 \overline{X}_n$$

- Chain transfer in radical polymerizations.

- A premature termination process that accounts for lower-than-expected M_n .
- Chain transfer agents may be monomer, initiator, solvent, or another substance. Sometimes we want to promote this!
- The rate of chain transfer is given by

$$R_{tr} = k_{tr}[\text{M}\cdot][\text{XA}]$$

- Chain transfer differs from termination in that it results in the formation of a new radical which can initiate a new polymer chain.
- ...

- Effect of the chain transfer on molecular weight.

- The degree of polymerization for a polymerization which has chain transfer is

$$\begin{aligned}\overline{X}_n &= \frac{R_p}{(2-a)(R_t/2) + R_{tr,M} + R_{tr,S} + R_{tr,I}} \\ &= \frac{R_p}{(2-a)(R_t/2) + k_{tr,M}[\text{M}\cdot][\text{M}] + k_{tr,S}[\text{M}\cdot][\text{S}] + k_{tr,I}[\text{M}\cdot][\text{I}]}\end{aligned}$$

where a is the fraction of chains which terminate by combination; 100% combination implies $a = 1$.

- **Chain transfer constant:** The ratio of the rate of chain transfer k_{tr} of the propagating radical with the substance to the rate of propagation of the radical. Denoted by C . Given by

$$C_M = \frac{k_{tr,M}}{k_p} \qquad C_S = \frac{k_{tr,S}}{k_p} \qquad C_I = \frac{k_{tr,I}}{k_p}$$

- **Mayo equation:** ...

- If a solvent otherwise works but has a very high chain transfer constant, you may not want to use it!

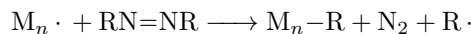
- The chemistry of chain transfer.

- Chain transfer to monomer.

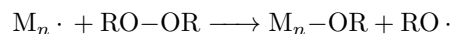
- C_M is generally small because the reaction usually involve breaking the stronger vinyl C–H bond.
- The largest monomer transfer constants are generally observed when the propagating radicals have very high reactivities, such as with ethylene, vinyl acetate, and vinyl chloride.
- We often have head-to-tail chemistry, but here we have some more head-to-head chemistry??
- Vinyl chloride's high value of C_M is also related to a reaction sequence that originates in a propagating center formed by head-to-head addition.
- C_M is really what places the upper limit on the polymer molecular weight. For example, the high C_M of vinyl chloride limits the M_n of PVC to 50,000-100,000, whereas with polyethylene, we can get into the millions.

- Chain transfer to initiator.

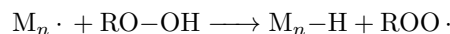
- Greater than chain transfer to monomer.
- However, transfer to initiator is governed by C_I , $[I]/[M]$, and $[I]$ is usually small (10^{-4} - 10^{-2} M).
- Azo initiator:



- Peroxides:



- Hydroperoxides:



- You have to take into account the nature of the polymer radical as well!

- Chain transfer to chain transfer agent.

- If transfer to the chain transfer agent dominates, then the Mayo equation simplifies to

$$\frac{1}{\bar{X}_n} = \left(\frac{1}{\bar{X}_n} \right)_0 + C_S \frac{[S]}{[M]}$$

where $(1/\bar{X}_n)_0$ is the value of $1/\bar{X}_n$ in the absence of the chain transfer agent.

- Reactivity of chain-transfer agent.

- Aliphatic hydrocarbons have strong C–H bonds, hence show low transfer constants.
- Benzene has an even lower transfer constant because of the strong C–H bonds in this aromatic and the instability of the aryl radical.
- The presence of more weakly bound hydrogen atoms in toluene, ethylbenzene, etc. leads to higher C_S values for these species when compared to benzene. The benzylic proton is readily abstracted because of resonance stabilization.
- Primary halides such as *n*-butyl chloride and *n*-butyl bromide behave similar to aliphatics and feature low C_S values; by contrast, the weak C–I bond in *n*-butyl iodide leads to an increased C_S value.
- Acids, carbonyl compounds, ethers, amines, and alcohols have higher transfer constants, corresponding to breakup of the C–H bond and stabilization of the radical by an adjacent O, N, or carbonyl group.
- The weak S–S bond leads to high C_S values for disulfides.
 - Note that disulfides are good chain transfer agents, but not good initiators because the radical is more stable.
- The high C_S values for carbon tetrachloride and carbon tetrabromide are due to the excellent resonance stabilization of the trihalocarbon radicals.
 - The weaker C–Br bond in CBr_4 leads to a substantial increase in C_S .
- Thiols have the largest C_S values of any known compounds, due to the weak S–H bond.
- Transfer agents...
- Use of the Mayo equation once again for moderation??

- Chain transfer to a polymer.

- Can create a propagation site anywhere along the polymer chain, which can lead to a branched polymer.
- Becomes important when the polymerization is carried out to high conversion.

- Example: polyethylene.
 - Two main types of branches: Long and short.
 - Long branches are formed as before from reactions between disparate chains.
 - Short branches outnumber the longer branches by 20-50 times. These form via **backbiting**.
- **Backbiting**: The radical site of propagation moving back a few carbons in a stable, six-membered ring. *picture*
 - Typical PE produced by radical polymerization contains 5-15...
 - May seem small, but has a massive effect on properties.
 - Gives you LDPE.
 - HDPE is *not* made free-radically! It's made using insertion catalysts, which we'll cover later.
- **Retardation and inhibition**.
 - Quinones are example inhibitors.
 - They inhibit the reaction until the concentration is fully consumed, then polymerization resumes.
 - Nitrobenzene is an example retarder.
- **Inhibitor**: An agent that *prevents* radical polymerization by reacting with the initiating and propagating radicals and converting them to nonradical species or radicals of reactivity too low to undergo polymerization.
- **Retarder**: An agent that *slows* radical polymerization by reacting with a fraction of the initiating and propagating radicals and converting them to nonradical species or radicals of reactivity too low to undergo polymerization.
- The class that Rowan thought would be virtual in a couple weeks *should* be in-person. All the rest should be as well!

Week 3

???

3.1 ???

1/16: • I was sick. See Callie's notes (PS2-PS3).

3.2 ???

1/18: • I was sick. See Callie's notes (PS3-2).

Week 4

???

4.1 Cationic Polymerization of Olefins

- 1/23:
- Recap of anionic polymerizations.
 - The double bond being attacked must be electron poor.
 - You usually want monomers to have conjugation (this helps make them electron poor).
 - Conjugation also helps stabilize the anion.
 - Your counterion and solvent are important.
 - This is the biggest difference between radical and ionic polymerization.
 - Even more important in today's discussion of cationic stuff.
 - The first living polymerization systems were anionic.
 - Living systems:
 - Can't have termination.
 - $R_i \gg R_t$.
 - **Chain end fidelity.**
 - PDI is close to 1.
 - You can control the MW, in particular via conversion (first order kinetics) or ratio of monomer to initiator.
 - These are the key points we need to take away from last time.
 - There is an exam coming up pretty soon! When??
 - **Chain end fidelity:** You have complete control of your ends.
 - Helpful if you want to make block copolymers or something.
 - We now begin cationic polymerization.
 - Cationic addition polymerization.
 - The mechanism is an attack on the carbocation by the nucleophilic monomer (electron *rich* double bond).
 - We want the *monomer* to be the most nucleophilic thing the carbocation sees, or we won't get the desired reactivity.
 - Competition comes from the anion.
 - Cl^- is quite nucleophilic, for instance; we want to cut down on this.
 - Our monomer needs to be quite a bit more nucleophilic, or all we get is termination.

- Some monomers which polymerize cationically.
 - Isobutylene and isoprene.
 - Best ones are those that have a lone pair, e.g., alkoxy groups.
- Characteristics of cationic polymerization.
 - We have to stabilize this very high-energy carbocation.
 - The obvious way is by delocalization, hence why styrene works well (even though it's not particularly nucleophilic, so we need a better ion in this case).
 - We'll talk more about isobutylene later; it's a slightly different case.
 - As we mentioned above, just like in the anionic case, counterion and solvent play an important role (actually a more important one).
 - There are a wide variety of modes for both initiation and termination.
 - Any oxygen in a backbone is a decent nucleophile.
 - Low temperature can prevent side reactions.
 - E.g., -70°C or even -80°C .
 - Lower temperature helps us not get over the higher activation barrier of certain side reactions.
- Regioselective electrophilic addition to substituted alkenes.
 - Markovnikov's Rule (1870) states that the addition of HX to an unsymmetrically substituted alkene results in the adduct in which H has bonded to the carbon bearing the greater number of hydrogens.
 - Initial protonation gives the most stable carbocation.
 - Stability of carbenium ions (carbocations).
 - Caused by **hyperconjugation**.
 - Example: A tertiary carbocation delocalizes the positive charge over *nine* other hydrogens.
 - Chemistry will go through *gymnastics* to get us to the most stable tertiary carbocation. This is coming up in a couple slides!
- **Hyperconjugation:** Delocalization that involves σ -bonded electrons rather than unshared/nonbonding- or π -electrons.
- What is required in a monomer and why?
 - Monomers require two things.
 1. The ability to form carbocations.
 2. The original monomer must be able to attack these newly formed cations.
 - This then requires the monomers to be nucleophilic (positive nucleus seeking). The monomer must contain electron-rich double bonds.
- Steric effects.
 - Sterics can hinder the polymerization of 1,2-disubstituted olefins. However, if the substituents are part of a cyclic structure, then the polymerization may occur.
 - This is because ring strain provides an additional driving force!
 - Steric considerations can be used to explain the difference in polymerization of similar monomer units.
 - Example: Norbornene has a less reactive double bond, but its sterics are far more favorable than with methylenenorbornene, even though the latter has an energetically favorable tertiary carbocation.

- The mechanism of cationic polymerization.
 - There are *many* ways by which this can take place.
- Initiation.
 1. Chemical methods.
 - (a) Two-electron (heterolytic).
 - i. Brønsted (protic) acids (proton donor).
 - ii. Lewis acids.
- All of these are relevant, but the ones in red are the ones we'll focus on. *More available in the slides.*
- Initiation generally consists of two processes.
 1. Ion generation or priming.
 - Brønsted acid: ...
 - ...
 - Aluminum¹: $2 \text{AlBr}_3 \rightleftharpoons \text{AlBr}_2^+ + \text{AlBr}_4^-$.
 - Notice all the “big, hairy counterions.”
 2. Cationation.
 - ...
- I. A. Brønsted (protic) acids.
 - We generate H^+ ions, and then the first H^+ attacks a nucleophilic double bond, generating the first carbocation in the **cationation** step.
 - Example of nucleophilicity:
 - N-vinyl carbazole $> \text{Cl}^- > \textit{iso}$ -butylene.
 - Everything has to do with *what's more nucleophilic*.
 - We can polymerize N-vinyl carbazole using HCl, but not *iso*-butylene!
 - This is why the counterion is important.
- I. B. Lewis acids.
 - This is why we use lewis acids more often — they would bond to that chlorine and go on.
 - Most of these are metal halides.
 - Examples.
 - AlCl_3 , BF_3 , SnCl_4 , ...
 - There are organometallic derivatives.
 - These are more soluble in the organic solvents we use, and hence better for that reason.
 - Examples: RAlCl_2 , R_2AlCl , R_3Al .
 - Most often, we need something in addition to the metal halide.
 - Takeaway: We need some kind of *donor* to give us these cationic species.
 - Example: If we add a touch of water to AlEt_3 , then we can generate H^+ and AlEt_3OH^- .
 - It is easy to separate the metal halides afterwards because we precipitate our polymer in a bad solvent for the polymer, filter out our polymer, and the catalyst stays in solution.
 - Depending on how important it is to separate the catalyst for your given application, maybe you do the precipitation procedure 4-5 times.

¹Historically, Webster's first dictionary misspelled the word as such; it was originally “aluminium,” like “potassium” or “calcium.” So that's why so many people pronounce it the Irish way.

- **Cationation:** This is the general attack of the cation by the monomer.
- Benzylic and tertiary halides can also be used to generate ions.
 - Benzylic *primary* carbocations are still super stable due to resonance.
- General initiation with Lewis acids.
 - A two-step process.
 - If step 2 is the slow step in initiation, then the rate of initiation is $k_i[M][Y^+(IZ)^-]$.
 - Of course, we don't know $[Y^+(IZ)^-]$, but we can work it out from the first equilibrium. This gives us the rate of initiation as

$$R_i = Kk_i[M][I][ZY]$$

- Exercise for the student: How do the kinetics change if step 1 is the slow step?
 - ...
- 2 Propagation.
 - A) Normal propagation: Addition.
 - B) Isomerization during propagation: 1,2-hydride or 1,2-methide shifts.
 - Driven by wanting to get tertiary carbocations.
 - Extent of rearrangements depend on two things.
 - 1) Relative stabilities of the propagating and rearranged carbocations.
 - 2) Relative rates of propagation and rearrangement.
 - Example: Little or no isomerization occurs with styrene, vinyl ethers, isobutylene because both (1) and (2) favor propagation.
 - However, this is not the case for some other hydrocarbon-substituted alkenes.
 - When you do this at the right temperature, you can get copolymers!
 - Less isomerization at higher temperatures, which favor propagation.
 - At lower temperatures, carbocation stability is king.
 - Example: β -pinene can be polymerized. *picture*
 - Release of ring strain from four-membered ring gives you a new repeat structure.
 - Another exercise for the student: Figure out how 4,4-dimethyl-1-pentene, ..., polymerize.
 - Rowan likes to use these on exams, so don't neglect this suggestion!!
- 3 Chain transfer and termination.
 - There are several ways in which chain transfer and/or termination can occur.
 - ...
- A. 1. Chain transfer to monomer.
 - Not much you can do about this.
 - The monomer would rather attack the positive charge, but it will, eventually, attack one of the protons that has gained a positive charge by stabilizing the carbocation.
 - NMRs of poly-isobutylene reveal lots of terminal double bonds.
 - General rate equation:

$$R_{tr,M} = k_{tr,M}[YM_nM^+(IZ)^-][M]$$
 - The chain-transfer constant to monomer is defined as the relative rates of chain transfer...
 - The Mayo equation holds true here as well!
- A. 2. Hydride ion abstraction from the monomer.

- Transfer the other way around! A proton from the monomer gets picked off by the chain.
 - B. 1. Chain transfer to the counterion.
 - This is a rearrangement of the propagating ion pair.
 - Kinetically does not depend on the concentration of the monomer.
- $$R_{ts} = k_{ts}[\text{YM}_n\text{M}^+(\text{IZ})^-]$$
- B. 2. Combination with counterion (spontaneous termination).
 - One of the main termination processes in TFA-initiated polymerization of styrene.
 - The counterion just directly bonds to our growing cation on the chain.
 - TFA \gg HOAc because the conjugate base is much more stable.
 - B. 3. Combination with a fragment of the counterion.
 - This is addition of an anionic fragment of the counterion to the polymer.
 - We cleave the weakest bond in every case.
 - Example: Since $\text{B-F} > \text{B-O} > \text{B-Cl}$, we append an OH preferentially over an F, but a Cl preferably over an OH.
 - ...
 - C. 1. Backbiting.
 - ...
 - C. 2. Chain transfer to polymer.
 - This is the carbocation of one polymer chain reacting with another polymer chain. Usually a hydride transfer process.
 - More important at higher conversions for the simple reason that there's more polymer around!
 - D. Other chain transfer and termination reactions (solvent, added components).
 - Everything can kill you, solvent included!
 - This is why you have to think about your system so carefully as you're designing it.
 - Rate.

$$R_{tr,S} = k_{tr,S}[\text{YM}_n\text{M}^+(\text{IZ})^-][\text{S}]$$

- Deliberately added compounds are good nucleophiles...
 - Can be used to functionalize your chain end if you do it right.
- Kinetics.
 - Assume steady-state conditions exist: At some time in the polymerization, the rate of initiation equals the rate of termination, i.e., every time one dies, another begins.
 - The total rate of polymerization is

$$R_p = \frac{K k_i k_p [\text{I}][\text{ZY}][\text{M}]^2}{k_t}$$

- Important takeaway: $R_p \propto [\text{M}]^2$.
- The number-average degree of polymerization comes down to the Mayo equation again. More specifically, derivation-wise,

$$\overline{X}_n = \frac{R_p}{R_t} = \frac{k_p[\text{YM}^+(\text{IZ})^-][\text{M}]}{k_t[\text{YM}^+(\text{IZ})^-]} = \frac{k_p[\text{M}]}{k_t}$$

- When chain breaking involves chain transfer to monomer, spontaneous termination, and/or chain transfer to solvent/impurity, then all these processes generated new propagating species.
- If we go through the whole derivation, we should get to the Mayo equation

$$\frac{1}{\overline{X}_n} = \frac{k_t}{k_p[M]} + \frac{k_{ts}}{k_p[M]} + C_M + C_S \frac{[S]}{[M]}$$

- Every time we add another chain transfer agent, we can just add another term!
- The kinetics if reaction with solvent or chain-transfer agent terminates the polymerization.
- R_p becomes

$$R_p = \frac{Kk_i k_p [I][ZY][M]^2}{\dots + k_t}$$

- This results in retardation.
- Comparison of some rate constants.
 - Some numbers for our edification.
- General trends for C_M (chain transfer to monomer) and C_S (chain transfer to chain-transfer agent).
 1. As k_p increases, C_M decreases:

$$C_K = \frac{k_{tr,M}}{k_p}$$
 2. C_S is higher for more nucleophilic S.
- Effect of reaction medium.
 - Solvent and counterion can play a significant role in cationic polymerization.
 - Example: Diluting $\text{BCl}_3 + \text{H}_2\text{O}$ with a bit of DCM gives us really nice polymerization.
- Activation energy of olefin polymerizations.
 - Generally, all olefin polymerizations are exothermic reactions on account of the conversion of π -bonds to σ -bonds, regardless of the initiator used.
 - However, the activation energy for the reaction...
 - All of this follows from the relationship between the rate constant and temperature given by the Arrhenius equation...
- Activation energy of olefin polymerizations: Rate.
 - E_p does not require a large activation energy.
 - Anionic olefin polymerization E_R is generally low and positive.
 - We can get a negative activation energy overall for the reaction if $E_t > E_i + E_p$.
 - Colder temperatures give us a faster reaction in this case!
 - Various polymerizations of styrene, some in which we want to heat it up to make it go faster, and some in which we want to cool it down to make it go faster.
- Activation energy of olefin polymerizations: Degree of polymerization.
 - We have that $E_{\overline{X}_n} = E_p - E_t$.
 - Here, lower temperature gives us higher molecular weight.
 - At -100°C , we've effectively switched off chain transfer to solvent.
 - Degrees of polymerization can increase orders of magnitude by switching off the chain transfer reactions at low temperatures.

4.2 ???

1/25:

- Today.
 - Finish up cationic.
 - Controlled/living free radical.
 - Start today, finish up on Tuesday.
 - Then the rest of Tuesday will be a review of our choice.
- Recap of cationic.
 - Monomers.
 - Nucleophilic.
 - Lot of conjugation.
 - Ones that form tertiary carbocations (e.g., isobutylene).
 - Good at low temperatures.
 - Shuts down side reactions, which have higher activation energies.
 - You can get rearrangements: Hydride (H^-) and methide (CH_3^-) shifts.
 - Often happens to get you to a tertiary carbocation.
 - Can be to relieve ring strain.
 - Nucleophilicity of the counterion is very important in determining rate of polymerization vs. rate of termination.
 - Large counteranions tend to be better (less nucleophilic).
 - Many ways for something to die. A lot more than in the anionic or free radical cases.
- We now pick up where we left off on Tuesday.
- Molecular weight distribution (dispersity).
 - At low conversion, all kinetic parameters ($[\text{M}]$, k_t , k_p , k_{tr}) are constant and molecular weight is constant.
 - The probability that a propagation ionic chain will propagate rather than terminate is given by

$$p = \frac{R_p}{R_p + R_t + R_{tr}}$$
 - It can be shown that

$$\overline{X_n} = \frac{1}{1 - p}$$
 - This is just Carothers' equation.
 - The derivation is in the book.
 - We also have

$$\overline{X_w} = \frac{1 + p}{1 - p}$$
 - The dispersity

$$D = \frac{\overline{X_w}}{\overline{X_n}} = 1 + p$$

has a limit of 2 when p is close to 1.

 - This is the most probable or **Flory/Schultz-Flory distribution**.
 - On account of the several chain-breaking reactions that can occur, D is to be broad, especially at high conversions.

- Differences between radical, cationic, and anionic polymerizations.
 - Simplifies learning: Just learn the conserved basics for all of them, and then learn the subtle differences between them.
 - Ionic polymerizations react dramatically to change the polarity and solvating ability of the solvent (ion pairs, solvent separated ion pairs, and free ions). Radical polymerizations do not.
 - Ionic polymerizations are more sensitive to impurities and rates of reaction are generally faster.
 - It is difficult to know sometimes whether a particular initiator system initiates a polymerization by a radical or ionic mechanism: Addition of certain radical scavengers such as the DPPH radical will halt radical polymerizations but not ionic polymerizations. (Note, not true for all radical scavengers.)
- Comparing radical and ionic polymerizations.
 - The cationic polymerization is described by the equations on the left below, and radical by the right.

$$\begin{array}{ll}
 R_p = \frac{R_i k_p [M]}{k_t} & R_p = k_p [M] \left(\frac{R_i}{2k_t} \right)^{1/2} \\
 R_p \propto R_i \propto k_p / k_t & R_p \propto (R_i)^{1/2} \propto k_p / k_t^{1/2} \\
 R_t \propto [M^+] & R_t \propto [M\cdot]^2
 \end{array}$$

- Some important differences.
 - Recall that we have the square dependence because the dominant mode of radical termination involves two radicals coming together (e.g., to form a single bond or via disproportionation to form a double bond).
 - Two positive charges will not come together to terminate!
- We do radical reactions at low radical concentration to cut down on termination because termination is so heavily dependent on radical concentration!
- Cationic rate of propagation is up to 10^4 faster than radical rate of propagation.
- Designing cationic living polymerizations.
 - Living gave us much more control for anionic; can we do something similar for cationic?
 - Challenge: Redesign so that propagating centers lower reactivity so that transfer and termination reactions are suppressed.
 - How do we eliminate chain transfer and termination?
 - Major problem: The distributed positive charge makes β -protons susceptible to nucleophilic attack (i.e., chain transfer to monomer). In order to prevent this transfer, we will need to stabilize the carbocation by donating electrons to it, which in turn reduces the charge on the β -protons. But we cannot make the monomer too stable, or it will not polymerize.
- Dynamic (reversible) “stabilization” of the reactive carbocation for better control.
 - How can we partially break a R–X bond without completely breaking it?
 - It should be noted that this equilibrium (as well as rates of propagation and transfer) is sensitive to a number of factors (e.g., temperature, solvents) and these can determine whether a polymerization is living or not.
 - Three general methods have been used to achieve living polymerizations.
 1. Initiator (HX)-mild Lewis acid, e.g., HI/I₂.
 2. Initiator (HX)-strong Lewis acids + nucleophile, e.g., 1,4-dioxane.
 - see blackboard picture from class

- 3. Initiator (HX)-strong Lewis acids + salt, e.g., ...
 - The initiator may be either an acid (HX) or their adducts with vinyl monomers.
- Example: Initiator (HX)-mild Lewis acid.
 - The mild Lewis acid (e.g., ZnX_2) is important.
 - If it is too strong, then uncontrolled polymerization occurs.
 - Vinyl ethers.
 - Other example.
 - It's really important that delocalization makes the carbonyl oxygen *always* the more nucleophilic species in an ester. *See picture from blackboard*
- Key points for cationic polymerizations.
 - Review of the major slides in the presentation.
- We now move onto controlled (“living”) polymerizations.
- Introduction.
- **Living polymer:** A polymer that retains its ability to propagate for a long time and grow to a desired maximum size while their degree of termination or chain transfer is still negligible.
- Basic properties.
 - ...
- If these basic properties are observed, then...
 - The MWD (dispersity, D) should correspond to a Poisson distribution, i.e., 1.
 - ...
- Living anionic polymerizations vs. standard free radical polymerizations.
- The difference between living and nonliving polymerizations.
 - An ideal free radical polymerization has termination by recombination has a broad distribution.
 - An ideal living polymerization has a spike in termination.
 - Anionic polymerization.
 - No termination.
 - No chain transfer.
 - All chains born at the same time and live until we kill them.
 - Free radical polymerization.
 - Termination present.
 - Chain transfer present.
 - All chains are born at different times and we have little control over their death.
 - Almost all free radical polymerizations can be done living. Then we're set!
- Standard radical polymerizations.
 - Free radical polymerization mechanism.
 - We need to remove coupling and disproportionation.
- How to reduce the concentration of the active species.
 - Use a reversible termination process.

- Have a stable dormant species that can break into stable radicals, react, and then give you more stable dormant species.
- We could get some bulk bimolecular termination, but if we keep radical concentration low with this reversible termination, then we should be pretty good!
- Reversible-deactivation radical polymerizations.
 - NMP, 1985.
 - First one.
 - ATRP.
 - RAFT.
- Stable free radical polymerization (SFRP).
 - We do need $Z\cdot$ to be a stable radical; if it reacts with itself, it will push the equilibrium toward the active radical via Le Châtelier Principle.
 - Stable radicals include nitroxide, trityl, and triazolinyll.
 - Nitroxide is stable because O–O bonds are notoriously weak.
 - Trityl is stable due to resonance delocalization and sterics.
 - Triazolinyll is sterics, too.
 - Nitroxide works the best by far.
- Nitroxide-mediated polymerization (NMP).
 - Heat up an alkoxyamine.
 - This works well, for instance, in the polymerization of styrene where we alternate back and forth between dormant and active to keep $[M\cdot]$ low.
- The persistent radical effect in living radical polymerization.
 - As a bit of bimolecular combination occurs, Le Châtelier's principle pushes the equilibrium back toward the dormant species, reducing further termination!
 - Essentially,
$$[M_n^*][X\cdot] = \text{constant}$$
 - If $[M_n\cdot]$ goes down, then $[X\cdot]$ goes up.
 - ...
- Nitroxides.
 - Most common one is TEMPO. You can just buy it.
 - The one on the far right appears to be the best.
 - You need fast initiation (low half-life); otherwise, much polymerization will occur before you've consumed all initiator, which is *not* a living characteristic.
- Polymerization of acrylates.
 - Poor control (broad D) with acrylates.
 - This is on account of the difference in rate of propagation of acrylates and styrene.
 - Acrylates: $k_p = 11\,000\text{ L mol}^{-1}\text{ s}^{-1}$ at $120\text{ }^\circ\text{C}$.
 - Styrene: $k_p = 1800\text{ L mol}^{-1}\text{ s}^{-1}$ at $120\text{ }^\circ\text{C}$.
 - Need to slow down the reaction in order to afford better control.
 - This can be done by the addition of free nitroxide.

- Takeaway: There are games to play with these kinds of reactions; if you think about it the right, you can basically work out what you need to do.
- Atom transfer radical polymerization (ATRP).
 - Pioneered by Sawamoto and Namcheski.
 - The metal pulls off a halide to create a radical that can polymerize, then can react back to a dormant species.
 - Very similar to NMP.
 - Requires a redox-active transition metal that can do 1-electron chemistry, e.g., $\text{Cu}^{\text{I}}/\text{Cu}^{\text{II}}$ (most common today), $\text{Ru}^{\text{II}}/\text{Ru}^{\text{III}}$, $\text{Fe}^{\text{II}}/\text{Fe}^{\text{III}}$.
 - The catalyst needs to have...
 1. Two oxidation states easily accessed by a 1-electron transfer;
 2. An affinity for halogens/pseudohalogens X;
 3. ...
- Copper-catalyzed ATRP.
 - Use $\text{Cu}^{\text{I}}\text{Br}(\text{L})$.
 - $\text{Cu}^{\text{II}}\text{Br}_2(\text{L})$ is our “persistent (metallo)radical.”
 - The equilibrium constant K is important here ($\sim 10^{-6}$) and provides an appropriate measure of the catalyst’s activity in a polymerization reaction.
 - If K is too small, then the reaction will not proceed.
 - If K is too large, then a large amount of termination will occur (too many radicals).
- Examples of monomers, initiators, and ligands used in ATRP.
 - Monomers.
 - Extensive.
 - Styrenes, acrylates, etc.
 - Initiators.
 - A lot of things with reactive species at the end.
 - Ligands.
 - Bidentate, tridentate, tetradentate, etc.
 - You just tune this until stuff works!
- If you do not select the correct initiator, ligand, and conditions for ATRP for a given monomer, the reaction will not be controlled.
 - There’s a crazy amount of work out there on ATRP, so start by looking for a paper that’s already done something similar and go from there.
 - Don’t use the first paper you find!
- Copper-catalyzed ATRP: Kinetics.
 - You only add 2-3 units at a time if you have a fast equilibrium.
 - You may also add hundreds of units each time with a slow equilibrium.
 - In this case, subsequent polymerizations will have noticeably lower monomer concentrations, so you get higher variation in molecular weights.
 - Assuming no termination and a fast equilibrium,

$$[\text{RM}\cdot] = \frac{K[\text{I}][\text{Cu}^+]}{[\text{Cu}^{2+}]} \qquad [R_p] = \dots$$

- Really nice straight plots...
- Copper-catalyzed ATRP (D).
 - We have
$$D = \frac{\overline{X_w}}{\overline{X_n}} = 1 + \left(\frac{[I]_0 k_p}{k_d [Cu^{2+}]} \right) \left(\frac{2}{p} - 1 \right)$$
 - Lower D : Low initiator concentration, higher conversions, rapid deactivation (high k_d and $[Cu^I]$) and lower k_p .
 - Proposed Cu^I/Cu^{II} species using bpy as a ligand.
 - The equilibrium is important for both rate and dispersity.
 - K increases with solvent dispersity and temperature.
 - ...
- Copper-catalyzed ATRP: Effect of ligand. *picture*
 - We're not expected to remember this, but this is a very useful slide.
 - "If you're doing an ATRP, you're welcome" - Rowan.
 - General trends: Copper complex activity increase (larger $k_a = k_{act}$).
 - tetradentate > terdentate > bidentate.
 - pyridine > aliphatic amine > imine.
 - Sterics; Me₆TREN is 10,000 times more active than Et₆TREN.

Week 5

???

5.1 ???

- 1/30:
- Review of copper-catalyzed ATRP ligand effects.
 - They're trying to prevent termination by lowering the radical concentration.
 - Essentially, the ligand plays an important role in the rate of activation.
 - Copper-catalyzed ATRP: Effect of initiator.
 - Initiator activity increase is related to the stabilization of the generated radical, so $3^\circ > 2^\circ > 1^\circ \dots$
 - Copper-catalyzed ATRP: ppm Cu.
 - Residual copper could have adverse effects if you're looking to make a medical product that will go into a person or a polymer to go into a piece of technology.
 - We typically need 0.1-1 mol% of copper relative to the monomer, so the product will contain a lot of it.
 - Thus, if we want to filter it out beyond just precipitating our polymer, we can throw in chelating agents or do fancier things, but that all adds cost and time to the process.
 - Termination does occur.
 - The rate of reaction depends on the ratio of $[\text{Cu}^+]/[\text{Cu}^{2+}]$ and not the absolute catalyst concentration.
 - So theoretically, we can go to much smaller catalyst loadings, as long as we keep that ratio high.
 - However, this is difficult to do because we need to regenerate Cu^+ using something other than radicals.
 - Copper-catalyzed AGET and ARGET ATRP.
 - AGET (Activators Generated by Electron Transfer) ATRP: Stoichiometric amounts of reducing agent added to the reaction mixture containing alkyl halides...
 - Wrapping copper wire around your stir bar will usually do the trick.
 - Essentially, we're just adding in a reducing agent.
 - ARGET (Activators ReGenerated by Electron Transfer) ATRP: Similar to AGET, but we use an excess of reducing agent which allows the use of much lower amounts of copper.
 - We can also use electrochemistry or photochemistry to reduce down.
 - These methods are much more commonplace now than traditional ATRP, *especially* if we're working toward biomedical devices.

- Reversible Addition-Fragmentation Chain Transfer (RAFT).
 - You use a standard free radical termination, but instead of having reversible termination, you have a reversible chain transfer process.
- Discovery of RAFT polymerization (1998).
 - RAFT polymerization controls chain growth through reversible chain transfer.
 - It can be achieved by the introduction of a small percent of a chain transfer agent into a conventional free-radical polymerization.
 - We most commonly use dithioester derivatives.
 - The R group...
- Steps in RAFT polymerization.
 - We use a standard initiator (e.g., AIBN).
 - We then have a step of pre-equilibrium or initialization.
 - Here, a polymer can add into the dithioester and kick out $R\cdot$ to begin a new polymerization.
 - Re-initialization: The growing of the new polymer from $R\cdot$.
 - Main equilibrium: Chain transfer back and forth through dormant chains bonded to dithioesters.
 - Various R groups for the chain transfer agent.
- RAFT: Snap shot of polymer chains.
 - A few dead chains, mostly dormant chains, and a few propagating chains.
 - Allows you to get a nice spike in molecular weight. Note that you might get a little tail on the low end due to dead chains.
 - All you have to do in the lab is throw in a bit of your RAFT pixie dust.
- RAFT equilibria.
 - The efficiency of a RAFT agent can be defined by C_{tr} . More active RAFT agents have larger C_{tr} . (C_{tr} should be at least 10; many are > 100 .)
 - We have that $C_{tr} = k_{tr}/k_p$ where

$$k_{tr} = k_{add}\phi = k_{add} \frac{k_{\beta}}{k_{-add} + \dots}$$

- Kinetics and livingness.
 - We won't go in depth into how to derive this stuff.
 - The rate of polymerization is...
 - We can define the **livingness** (how much is dormant or growing vs. dead).

$$L = \frac{[CTA]_0}{[CTA]_0 + 2f[I]_0(1 - e^{-k_d t})(1 - f_c/2)}$$

- The number of chains produced in a radical-radical termination event.
- $f_c = 1$ means 100% termination by combination, whereas $f_c = 0$ means 100% termination by disproportionation.
- Monomers with high propagatino rates (such as acrylamides) and initaotors with high efficiency or high decomositio rate lead to fast polymerization rate while keeping low initiator concentration.
- An optimal RAFT system requires a high rate of radical generation (considering k_d , for instance, by using thermal initiator at $T >$ their ten-hour half-life) and/or solvent induced acceleration.

- A large polymerization rate permits shorter polymerization time or lower amounts...
- Reactivity of the monomers and their propagating radicals.
 - Monomers can be classified into two general groups.
 - More “activated” monomers (MAMs).
 - Conjugated double bond (e.g., styrene, methyl methacrylate, acrylamide, acrylonitrile, ...).
 - Reactive monomer.
 - Less reactive propagating chains.
 - This means that poly(MAM) is a relatively good homolytic leaving groups, and as such, the more active RAFT agents provide good control. Less active RAFT agents have lower C_{tr} and provide poor control.
 - Less “activated” monomers (LAMs).
 - Saturated carbon or oxygen/nitrogen.
 - ...
- Relationship of RAFT agent and monomer.
 - Optimal control in RAFT polymerization requires choosing an appropriate RAFT agent for the monomer(s) to be polymerized.
- Z group impacts the reactivity of the RAFT agents.
 - How reactive is C=S to attack?
 - The reactivity can be qualitatively understood in terms of the importance of zwitterionic canonical forms. The lone pair delocalization with the C=S reduces its double bond character and stabilizes the RAFT agent relative to the radical intermediate.
 - The reactivity of the RAFT agent can be increased if the electron density of the lone pair is reduced by delocalization everywhere.
- Relationship of RAFT agent and monomer; the role of the Z group.
 - Z modifies the rate of addition of propagating radicals (k_{add}); it can be altered by 5 orders of magnitude.
 - Z alters the stability of the radical intermediate; the rate of fragmentation k_{-add} .
 - Z should not cause any side reactions.
 - For xanthides...
 - If Z is strongly electron withdrawing, then the C=S can react directly with the monomer (e.g., a hetero Diels-Alder) or nucleophilic attack.
 - Guidelines for selection of the Z group of RAFT agents (ZC(=S)SR) for various polymerizations.
 - ...
- Relationship of RAFT agent and monomer; the role of the R group. *picture*
 - For an effective RAFT agent, R· should be...
 - A really good leaving group with respect to the propagating radical [P·] ($\phi > 0.5$);
 - Be able to reinitiate the polymerization efficiently ($k_{iR} > k_p$), otherwise retardation occurs. Related to the stability of R·.
 - Guidelines for selection of the R group of RAFT agents.
 - See Figure ??
 - A dashed line indicates only partial control (control of molar mass but poor control over dispersity or substantial retardation in the case of VAc, NVC, NVP).

- Radical stability is important in determining the fragmentation rates.
- Steric factors play a role.
- Polymerization of 1,1-disubstituted monomers (e.g., methyl methacrylate, methacrylamides) which result in a tertiary $P_n \cdot$...
- However, polymerization of monomers with high k_p are best controlled with primary and secondary R groups. Tertiary radicals are inefficient at reinstating polymerizations since $k_{i,R}$ is often lower than k_p .
- Just because someone gets it to work for styrene doesn't mean it'll work for everything.
- RAFT CTA choice is everything.
 - A table that summarizes choices.
- Synthetic potential of RAFT.
 - You can do chemistry on your RAFT chain ends.
 - Example: You can react a diene with the C=S bond in a hetero Diels-Alder reaction.
- Targeting molecular weights with RAFT.
 - Your number average molecular weight is

$$\frac{\text{Total monomer concentration}}{\text{Total initiated-unit concentration}} \times \text{Conversion} \times \text{Monomer molar mass} + \text{CTA molar mass}$$
 - Thus, ...
- Key points.
 - Understand what a living polymerization is.
 - What does that mean for the resulting polymerization?
 - Standard living (ionic) and controlled living (reversible step).
 - Know and understand RAFT, ATRP, and NMP; know how to decide which one you will use.
- Midterm.
 - Know common monomers, know common polymers, know how they can be initiated.
 - Know how to draw reaction mechanisms.
 - There's at least one question that might require a calculator.
 - Implication: There's a kinetics question coming.
 - For the grad level course, papers are 20% of the exam! Don't ignore them!!
 - The kinetics from today's lecture won't be there.
 - Focus on intro, cationic, anionic, and free radical classes.

5.2 ???

- 2/1: • I was at ??

Week 6

???

6.1 Ring-Opening Polymerizations

2/6:

- Relevant reading: Odian, Chapter 7.
- **Ring-opening polymerization:** The conversion of cyclic monomers into polymers via a ring opening process. *Also known as ROP.*
- Introduction.
 - The impact of size is very important in ROP.
 - You need a way to *kinetically* open the ring.
 - There can be an *equilibrium* between macrocyclic and linear species.
 - This equilibrium is big.
 - In order to induce polymerization, the equilibrium has to be driven toward the linear side.
 - Not every ring can be polymerized; one of the big things in this class is learning how to determine which rings can be polymerized.
 - A monomer require ring strain (thermodynamic) and a nucleophilic site (kinetic).
- Monomers that can be polymerized via ROP.
 - We'll talk about most of the monomers on this slide.
 - First half: Polymerizing ethers and ester.
 - Then different ones.
 - Poly- ϵ -caprolactam is nylon!
 - There is a polymer called polysulfur that is just a bunch of sulfur atoms in a chain!
- General mechanism (two basic types).
 1. Cationic ROP.
 - We get a positive charge (e.g., oxonium) and then the charge transfers after nucleophilic attack.
 2. Anionic ROP.
 - The anion on the growing chain attacks the monomer.
- Major driving force: Ring strain.
 - This is a more thermodynamic factor and is the relative stability of the cyclic monomer vs. linear polymer.

- We *can* use entropy to drive this, but most often, we take $\Delta H \ll 0$.
- ...
- Bond angle distortion.
 - This is the primary way to drive polymerization.
 - 3- and 4-membered rings have the most distorted bond angles and are very reactive toward polymerization.
 - **Transannular strain** increases strain in an 8-membered ring.
 - 8-membered rings are actually *great* to polymerize.
 - A 6-membered ring is the most thermodynamically stable; except for a *few* known exceptions, these do not polymerize.
 - Example: Trioxane; the oxygens get us away from ideal bond angles because of their lone pairs!
 - Thus, *en toto*, the thermodynamic feasibility for polymerization in terms of ring number is

$$3, 4 > 8 > 5, 7 \gg 6$$

- Kinetic factors.
 - Require functionality (a nucleophile) in the ring, which allows propagation to occur.
 - The rate of polymerization depends on both the reactivity of the monomer and active species.
 - The question is, “which is more important?” The *nucleophilic* nature of the monomer and the *electrophilic* nature of the active species.
 - Aziridine is more nucleophilic than cyclopropoxide because the nitrogen is less electronegative than the oxygen.
 - In general, the higher the basicity of the parent monomer, the lower the reactivity of the active species derived from this monomer toward the standard monomer.
 - The rate constant k_p of homopropagation overall decreases as the nucleophilicity of Z in the monomer increases because the activity of the active species controls the rate of homopropagation.
 - This tells us that in the transition state, the bond breaking is more advanced (it’s driving the polymerization) than the bond making.
- Thermodynamics of polymerization of cyclic ethers and acetals.
 - Observe that 3- and 4-membered cyclics are comparable to those for alkenes.
 - Substitution on the ring generally decreases tendency to polymerize because of sterics.
 - 6-membered rings are generally difficult to polymerize.
 - Generally, the larger the ring, the lower the entropic cost.
- Comparison to olefin chain and step-growth polymerization.
 - Initiators required, similar to cationic and anionic initiators used in olefin polymerizations.
 - Shows similar characteristics to those described for ionic olefin polymerizations: Effect of solvent, counterion, propagation by different species (covalent, ion pair, free ions).
 - Growth process similar to chain polymerization in that only monomer adds to growing chain.
 - However, rate constants are closer to step-growth polymerizations and there is a slower build up of molecular weight...
 - This means that it’s easier to get living polymerizations with this technique because the reactions are less fast.

- The following kinetics are almost identical to the alkene case.
- Thus, Rowan will focus more on the *chemistry* than the *kinetics*.
- Chemistry of ROPs.
 - Very similar to step-growth polymerizations, but with no condensation product.
 - ...
 - In THF, the positive charge converts oxygen into a good leaving group and we just do S_N2.
 - Aside: You should never use a strong cation in THF solvent because the cation will just polymerize it!
- Cationic Ring-Opening Polymerization (CROP).
 - Propagation with a *cationic* species.
 - General characteristics.
 - The cyclic monomers require a nucleophilic site. In general, the nucleophilic site in ROP is more nucleophilic than a double bond.
 - Shows most of the characteristics of vinyl cationic polymerization.
 - ...
- Initiation.
 - Similar to cationic!
 - Use a Brønsted (protic) acid.
 - Stable organic salts work well.
 - Lewis acids can also help out.
 - You can also do initiation with a covalent compound.
 - Use strong alkylating or acylating agents.
 - Depends on the nature of the nucleophile in the ring.
 - RBr is good for amines and oxazolines.
 - ROSO₂CF₃ is good for acetals or ethers (O); it's a *very* good **methylation agent**.
 - This also means that you should not use an alkylating agent in THF!
 - We can think of CF₃SO₃ as an almost *dormant* species, because once it is bound to a chain end, it can just react with THF again!
- Propagation.
 - Three possible propagation mechanisms.
 1. Activated chain-end (ACE) mechanism (ionic species).
 2. Activated chain-end (ACE) mechanism (covalent species, pseudocationic).
 3. Activated monomer (AM) mechanism.
 - Which propagation mechanism occurs depends on the nucleophile in the ring and the initiator.
 - Examples of ACE and AM.
 - Both ACE and AM can occur simultaneously in the polymerization process. The AM mechanism (which reduces the amount of cyclics formed during polymerization) can predominate if the ratio of [Monomer]/[HO[−]] is kept low, i.e., slow addition of monomer to the reaction mixture.
 - We can get backbiting in AM mechanisms; polymerizing ethylene oxide cationically just gets you a bunch of dioxane, which is just a thermodynamic well that you fall into.
 - Adding a small smidge of alcohol in will preferentially react with the activated monomer.
 - Not the best ever; ACE will still be actively generating dioxane. But not bad.

- Transfer and termination.
 - Almost all analogous to cationic alkene polymerization.
 - Chain transfer to polymer.
 - Probably the most common mode of transfer in this case.
 - If intermolecular, we'll get some mixing of molecular weights as chains exchange their growing fragments.
 - We can get intramolecular backbiting, too.
 - Termination by irreversible recombination.
 - Three different nucleophiles can react with the active cationic species.
 1. Monomer (leads to propagation).
 2. ...
 - Termination with polymer.
 - We can get branched structures that are fairly stable and don't react further.
 - Termination by counterion.
 - Termination by reactions with other compounds in the system: Solvent and impurities.
 - Termination by water does occur. However, it is less important than in vinyl cationic polymerization on account of the cyclic monomer being more nucleophilic than the vinyl monomer.
 - Termination by reaction of more reactive species existing in equilibrium with stable onium species.

6.2 ???

- 2/8: • I was at the CCRF national scholars luncheon.

Week 7

???

7.1 Coordination/Insertion Polymerization

- 2/13:
- Adding a coordinating metal chain to the end of the polymer, and then the metal activates the monomer.
 - **Coordination polymerization:** A polymerization in which the growing polymer is bound to a metal atom and that insertion of the monomer into the metal-bound polymer is preceded by, and presumably activated by, the coordination of the monomer with the metal. *Also known as insertion polymerization.*
 - Introduction.
 - Both olefin polymerizations and ROPs can be carried out by insertion polymerization.
 - For asymmetric monomers, there are two possible modes of insertion (primary/1,2 and secondary/2,1).
 - It's mainly the d orbitals of transition metals that can do this.
 - Free radical polymerization of ethylene.
 - Does not result in a linear change; gives LDPE with many short chains due to backbiting.
 - 5-15 n -butyl chains and 1-2 ethyl, n -amyl, and n -hexyl branches per 500 monomer units.
 - Produced via backbiting.
 - Short chain branches outnumber the longer branches by 20-50 times.
 - Produced via chain transfer to polymer.
 - Quite a broad dispersity (PD 3-20).
 - Low glass transition temperature and melts (40-60%) at 105-115 °C.
 - We *cannot* make HDPE using free radical polymerization.
 - Free radical “polymerization” of polypropylene?
 - Reacting propylene with free radicals does not yield polymers, only oligomers.
 - We get a stable allyl radical.
 - Some grocery store bags are LDPE (that's why they break). Good HDPE can stop a bullet.
 - Olefin polymerization with coordination catalysts.
 1. Polymerization of ethylene.
 - Ziegler-Natta catalyst produces linear polyethylene (HDPE).

- Ziegler and Natta won the Nobel Prize for this!
- 2. Can polymerize propylene and other α -olefins.
 - Copolymer of hex-1-ene and ethylene produces linear low-density polyethylene (LLDPE); like LDPE but requires less energy to produce.
- 3. Specific tacticity can be achieved with α -olefins.
 - Isotactic polymers.
 - Syndiotactic polymers.
- 4. Homogeneous and heterogeneous catalysts.
 - Solution phase vs. pumping stuff over a solid catalyst.
- Work on polymerizing propylene was nearly abandoned prior to the discovery of Ziegler-Natta catalysts!
 - Take away: Don't abandon ideas...
- Ziegler-Natta polymerization of non-polar olefin monomers.
 - The discovery was completely serendipitous.
 - This is a really good instance of keeping an open mind; they were able to realize that what they had found was way more cool than what they were working toward.
 - Book: *The Chain Straighteners*.
 - They cleaned the bomb really well, but they *needed* some of the previous day's contaminant (AlEt_3) to initiate the reaction.
 - Present-day *super-active* or *high-mileage* system: A heterogeneous catalyst.
 - Ball milling...
 - With MgCl_2 support, the catalyst produces as much as 7 kg PE/hr.
 - Ziegler won for polyethylene polymerization; Natta realized that it could be done with polypropylene.
- Reaction of the Ziegler-Natta components.
 - Two different models.
 - Important things to remember: Unoccupied/vacant orbital at the catalyst site, coordination to the monomer.
- Tacticity in polymers.
 - Isotactic: Chain ends must add to the same face of every double bond.
 - Syndiotactic: Hitting opposite faces in succession.
- Mechanistics.
 - We believe that tacticity is controlled by the nature of the catalytic site: So this is a catalyst site to control mechanism.
 - Thus, for isotactic addition, we need a chiral catalyst site.
 - Let's look at the surface of this heterogeneous (solid) catalyst and the gaseous monomer it reacts with.
 - Titanium likes to be hexacoordinate.
 - The way the titaniums bond to each other makes some have D_3 /paddlewheel symmetry in a sense, and others be enantiotopic to that.
 - Broad MWD is usually observed for heterogeneous Ziegler-Natta systems (5-30 have been reported).

- Equivalent homogeneous system uses vanadium. This does syndiotactic PP.
 - Rowan explains the alternating growth mechanism from CHEM20200Notes.
 - The metal will react with the carbon bearing the R group in the monomer.
- Great summary of homogeneous vs. heterogeneous.
 - ...
- Termination of chain growth.
 - ...
- Polymerization of dienes with Ziegler-Natta catalysts.
 - Selective polymerization of butadiene, for instance.
 - Four different stereoregular polymers...
- **Metallocene**: A positive metal ion sandwiched between two negatively charged cyclopentadienyl anions.
 - Ziegler-Natta was the first generation.
 - Metallocene advantages.
 1. Over 100-fold more reactive than heterogeneous Z-N initiators.
 2. Very high molecular weight polymers.
 3. Single site initiators.
 - Polymer with better stereo- and regio-control.
 - Narrower molecular weight.
 - Zr is bigger than Fe, thus better and more accessible active site.
 - The indenyl anion is another aromatic anion; binding two of these together with an **ethylene bridge** forms a bulky ligand that can be used to help direct the monomers to react in the correct orientation.
 - These produce isotactic PP very well.
 - We activate the catalyst by ripping off the chlorines and alkylating.
- Mechanism.
 - Polymerization alternates between the two different ligand positions.
 - The double bond is inserted between the metal and the polymer through a 4-membered transition state.
 - ...
- If you could force the polymer to attack the opposite faces of the olefin alternatively, then you can produce syndiotactic polymers.
 - Another catalyst does this!
- Oscillating metallocenes.
 - Without the tethering group, the aromatic anions rotate.
 - But they rotate relatively slowly between their conformers, so we get stereoblock copolymers.
- Altogether, metallocenes have active sites that are fairly constrained, which is good for controlling tacticity but not good for bigger monomers.
- *ansa*-Cyclopentadienyl-amido initiators.

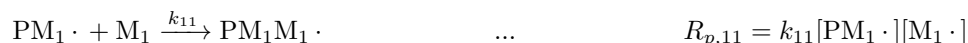
- ...
- Phenoxy-imine chelate initiators.
 - R^1 is usually phenyl or substituted...
- Issue: Most of these catalysts are very oxo-philic, so α -olefins work, but basically anything else doesn't.
- Potential solution: α -diimine chelates of late transition metals.
 - Late transition metals (e.g., Ni and Pd) are less oxophilic. However, such systems tend to have low activity (forming only oligomers) on account of extensive β -hydride transfer.
 - Propagation and branching mechanism.
- We now move into olefin metathesis.
- Olefin metathesis (ROMP, ADMET).
 - We're essentially breaking two old double-bonds and forming two new double bonds.
- Catalysts.
 - Ziegler-Natta-type initiators can be good.
 - We have a four-membered transition state (hotly contested, but eventually proven and later modeled by Yves Chauvin — one of the 2005 Nobel Prize people, along with Schrock and Grubbs).
 - Schrock, Grubbs I, and Grubbs II covered.
 - Nowadays, Aldrich sells specialized versions of these that have been tuned and tailored for various applications.
- Mechanism for how these catalysts work.
 - ...
- Commercial olefin metathesis polymers.
 - Story about dicyclopentadiene from Bob Grubbs.
 - Materia was the company.
 - It was a very durable polymer.
 - He got baseball players to fund it by making a baseball bat and then one decided to bash it against the ground and it didn't break, so they all ventured in.
 - Rate of polymerization vs. rate of backbiting.
 - You have to stop the reaction very quickly.
 - You can graft things off the side of polymers.
- ROMP is by far the dominant method of olefin metathesis, but it's not the only one.
- Acyclic Diene Metathesis Polymerization (ADMET)¹.
 - This is a condensation polymerization.

¹Sounds like Anderson misnamed this!

7.2 Copolymerization

- 2/15:
- Copolymerization why does this matter?
 - Copolymers are polymers made from more than one monomer.
 - Wide range of property profiles can be achieved from only a few monomers... by making block, graft, or statistical copolymers.
 - This section...
 - Copolymerization.
 - Polymerization of more than one monomer at the same time.
 - You almost never get 50/50, though, because one monomer will be more reactive than the other (or because they are introduced in different concentrations).
 - Step-growth copolymerization: Many step-growth polymers are copolymers. As the polymerization is carried out close to 100% (for high MWt), then the overall composition of the polymer is usually the same as the feed composition.
 - Chain copolymerization: As (co)polymers are formed throughout the polymerization then copolymerization is more complicated. This is the focus on this section.
 - Chain copolymerization.
 - For chain polymerization, the polymer chemical microstructure (i.e., the amount and placement of the different monomers) depends on *both* relative monomer concentrations and relative reactivities. Note that depending on the reactivity of the monomers, the monomer feed can change during the reaction.
 - Now there's **composition drift**, too.
 - At low conversions, the more reactive monomer will be incorporated more often. At high conversions, the less reactive monomer will be more left over and its excess of concentration means that it will start to be incorporated more.
 - Types of copolymers made by copolymerization of two monomers.
 - Statistical and random copolymers: A copolymer consisting of macromolecules in which the sequential distribution of the monomeric units obeys known statistical laws.
 - Note: An example of a statistical copolymer is one consisting of macromolecules in which the sequential distribution of monomeric units follows Markovian statistics.
 - Truly random copolymers are formed if the probability of finding a given type monomer residue at a particular point in the chain is equal to the mole fraction of that monomer residue in the chain (Bernoullian [zero-order Markov]).
 - All randoms are statistical; not all statistical are random.
 - Alternating copolymer: An alternating copolymer is a copolymer comprising two species of monomeric...
 - What determines microstructure?
 - ...
 - Reactivity of monomers in copolymerization cannot be determined by the knowledge of the homopolymerizations of both monomers.
 - Some monomers are more reactive in copolymerization than would be indicated by their rate of homopolymerization.
 - Some monomers that cannot polymerize *at all* on their own polymerize beautifully with others.

- Think bulky monomers that can't react with each other but can be strung together by smaller molecules.
- Some monomers that cannot...
- **First-order Markov** or **terminal model** of copolymerization: Assumes that the chemical reactivity of the propagating chain depends only on the nature of the monomer units at the chain end (and is independent of what P is).
- There is **self-propagation** and **cross-propagation**.
 - Monomers (at growing chain ends) reacting with like monomers vs. monomers (at growing chain ends) reacting with unlike monomers.
- Assumptions (to make things not ridiculously complicated).
 - ...
- You can take this a step further by considering the effect of the next to last repeat unit. This is called the **penultimate** control mechanism.
 - Good to know and be aware of, but there are a lot more equations.
 - So in this course, we will focus only on the terminal model.
- Copolymerization equation derivation.
 - Goal: Find a way to express the conversion of M_1 and M_2 into the polymer over time.
 - Recall the four propagation equations.



- This means that the rate of M_1 consumption (rate of its addition into the polymer) is given by

$$\frac{d[M_1]}{dt} = R_{p,11} + R_{p,21} = \dots$$

and

...

- It follows that

...

- If we make a quasi-steady state assumption that the total concentration of radicals is constant, then the rate of cross-over between different types of terminal units is equal. Mathematically,

$$\frac{[PM_1 \cdot]}{[PM_2 \cdot]} = \frac{k_{21}[M_1]}{k_{12}[M_2]}$$

- Combining the previous two equations, we obtain

$$\frac{d[M_1]/dt}{\frac{d[M_2]}{dt}} = \frac{[M_1]}{[M_2]} \cdot \frac{(k_{11}/k_{12})[M_1] + [M_2]}{(k_{22}/k_{21})[M_2] + [M_1]}$$

- We can measure monomer concentrations over time using NMR or something, so this allows us to get the rate constant ratios in the above equation.
- These rate constant ratios are formally known as **reactivity ratios** and tell you the ratio of self-reactivity compared to cross-reactivity.
 - For binary systems, r_{ij} may be shortened to r_i and r_{ji} may be shortened to r_j .
 - Thus,

$$r_1 := \frac{k_{11}}{k_{12}} \qquad r_2 := \frac{k_{22}}{k_{21}}$$

- Example: If $r_1 < 1$, then $\text{PM}_1 \cdot$ preferentially adds to M_2 .
 - If $r_1 > 1$, then $\text{PM}_1 \cdot$ preferentially adds to M_1
 - If $r_1 = 0$, then that monomer cannot homopolymerize.
 - Note that reactivity ratios — like rate constants — depend on temperature, solvent, etc.
- Composition vs. feedstock.
 - All of the previous equation was based on concentration.
 - It can be useful, instead, to describe the *mole fraction* of the monomer/repeat unit in both the feedstock and polymer (instead of concentrations).
 - F_1 is the mole fraction of M_1 in the polymer.
 - This means that $F_1 + F_2 = 1$.
 - f_1 is the mole fraction of M_1 in the feed.
 - This means that $f_1 + f_2 = 1$.
 - Thus,

$$F_1 = 1 - F_2 = \frac{d[\text{M}_1]/dt}{d[\text{M}_1]/dt + d[\text{M}_2]/dt} \qquad f_1 = 1 - f_2 = \frac{[\text{M}_1]}{[\text{M}_1] + [\text{M}_2]}$$

- Combining these equations with the previous, concentration-based result, we get

$$F_1 = \frac{r_1 f_1^2 + f_1 f_2}{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2} \qquad \frac{F_1}{F_2} = \dots$$

- Either of these is referred to as the **Mayo Lewis equation**.
- Microstructure of copolymers.
 - The copolymer composition equation describes the overall composition of the copolymer but does not say anything about exact arrangement of the two monomers along the polymer chain.
 - It is important to note that unless $r_1 = r_2 = 1$, the placement is *not* random and should properly be considered *statistical*.
 - The microstructure of the copolymer is defined by the distribution of the various lengths of M_1 and M_2 sequences, the **sequence length distribution**.
 - The mole fractions of $(N_1)_x$ and $(N_2)_x$ of forming M_1 and M_2 sequences of length x are...
 - No need to focus on this mathematically.
 - Visually, however, the equations tell us that if $r_1 = r_2 = 1$ (i.e., $f_1 = f_2$), then the probability of finding repeats of length x decreases exponentially.
 - In cases where r_1 is big and r_2 is small, most M_2 's will be by themselves and there will be a more stretched out exponential distribution of M_1 .
 - In cases where both are small, both M_1 and M_2 will very much most commonly appear by themselves. This gives us an **alternating copolymer**.
- Reactivity ratios.
 - A few notes.
 - Get comfortable with this slide by any means necessary!!
 - “Learn it, study it, climb into bed and sleep with it if you have to.”
 - This slide makes everything in this presentation make sense.
 - Repeats some stuff from above.
 - Both ratios are needed to characterize the system: Although r_1 is descriptive of the radical $\text{M}_1 \cdot$, it also depends on the identity of $\text{M}_2 \cdot$; ...

- ...
- Determining reactivity ratios.
 - We can use the mole fraction equation.
 - We can control the monomer feed ratio f_1, f_2 , so the key is then to measure the copolymer composition F_1, F_2 .
 - To get F , we use analytical techniques that allow us to determine the amount of each repeat unit.
 - Examples: Elemental analysis, NMR, MS, FT-IR, UV, etc.
 - Remember, it is important to properly purify up the sample to remove solvent, initiators, monomers, etc.
 - Back in the day, we could use the Mayo-Lewis method, but it was wildly inaccurate; no one does it any more.
 - We use a lot of nonlinear methods and curve fitting.
 - Look at sterics in the example!
- Reactivity ratios.
 - There are some tables in books of reactivity ratios and the products for selected copolymers at given temperatures.
 - There aren't many examples where both $r_1, r_2 > 1$; thus, for block-copolymers, we probably need a different method.
 - Note that $0 < r_1 r_2 < 1$ in general.
- Type of copolymerization behavior.
 - When $r_1 r_2 = 1$, we call this an **ideal copolymerization**.
 - This is when the propagating species, $\text{PM}_1 \cdot$ or $\text{PM}_2 \cdot$, show the same preference for adding one or the other of the two monomers, i.e.,

$$\frac{k_{22}}{k_{21}} = \frac{k_{12}}{k_{11}} \quad \text{or} \quad r_2 = \frac{1}{r_1}$$

and the relative rates of incorporation of the two monomers into the copolymer are independent of the propagating species. Using prior copolymerization equations for an ideal copolymerization, we have ...
 - Note...
 - A special case of ideal copolymerization: When $r_1 = r_2 = 1$.
 - Here, the copolymer composition is the same as the monomer feed.
 - We can calculate that $F_1 = f_1$ from the equation.
 - This is true **random** or **Bernoullian** behavior.
 - In an ideal copolymerization when $r_1 \neq r_2 \dots$
 - As r_1 increases, then F_1 increases.
 - It becomes harder to produce copolymers containign both monomers as the difference in r_1, r_2 increases.
 - Only if r_1, r_2 are not too different, e.g., r_1 is 0.5-2 can polymers be obtained with an appreciable amount of both monomers.
 - If $r_1 r_2 = 0 \dots$
 - If, in addition, neither r_1 nor r_2 is greater than 1, then the propagating species prefers to react with the other monomer. This leads to

...

- Examples are rare, but they do exist.
 - Example: Radical polymerization of stilbene and maleic anhydride.
- Block copolymers.
 - Even rarer.
 - The example given is very hard to do.
- Most copolymerizations are $0 < r_1 r_2 < 1$.
 - The tendency toward alternation and the tendency away from ideal behavior increases as $r_1 r_2$ moves from 1 to 0.
 - For the cases where both $r_1, r_2 < 1$, ...
- Radical olefin copolymerization.
 - Reactivity ratios are kinetic in origin and are therefore a reflection of transition state of the reaction.
 - Effect of reaction conditions.
 - Reaction medium: Generally, solvent does not have a big effect on reactivity ratios.
 - Temperature: If the polymerization is irreversible, then temperature does not have a large effect on reactivity ratios in radical copolymerization.
 - The variation with T will depend on the difference in propagation activation energies.
 - As the activation energies of radical propagation are small and similar...
- Relation of reactivity to chemical structure.
 - The reactivity ratios can be...
 - We can examine the reactivities of the radicals and monomers by looking at the rates of cross-propagation (i.e., the rate of radical 1 reacting with monomer 2, which is k_{12}).
 - Values of cross-propagation constants k_{12} ($\text{L mol}^{-1} \text{s}^{-1}$) for four monomer-radical combinations.
 - Resonance stabilization has more of an effect on the reactivity of the radical than the reactivity of the monomer.
 - Resonance: Consider species that either have or have not resonance stabilization (rs).
 - A stabilized radical reacts with a stabilized monomer to form a stabilized radical.
 - ...
 - The last one is by far the most favorable reaction.
 - Steric effects — the counterpart to rs.
 - The *cis* option is super destabilized.

Week 8

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8.1 ???

2/20:

- Relation of reactivity to chemical structure.
 - Polar effects: Alternation.
 - Enhanced reactivities are observed between certain pairs of monomers on account of subtle radical monomer interactions, which can lead to alternating tendency in such polymerizations.
 - This is observed between copolymerization of electron rich and electron poor double bonds.
 - Example: Styrene (electron-rich) and maleic anhydride (electron-poor).
- Reactivity ratios.
 - Many ways to visually represent these, such as **reactivity triangles**.
 - Shows that as you get greater difference between electron rich and electro poor, $r_1 r_2$ approaches 0.
- Reactivity ratios summary.
 - A great visual description of everything discussed last time.
 - Very concise, too!
 - Emphasis: “Random” and “statistical” are *not* interchangeable!
- Composition drift.
 - The copolymerization equations give the instantaneous copolymer composition.
 - However, in all copolymerizations except **azeotropic copolymerizations**, the comonomer feed changes in composition as one of the monomers gets incorporated preferentially into the polymer. This leads to a drift in monomer composition to the less reactive monomer.
 - There’s a kind of hexagonal (view it three-dimensionally!) chart that summarizes all this.
- **Azeotropic** (copolymerization): The formation of a copolymer for which the overall composition of copolymer monomeric units equal to the composition of the feed.
- Summary.
 - The key parameters in copolymerization are the reactivity ratios, which influence the relative rates at which a given radical will add to the same monomer vs. a comonomer.
 - The copolymerization equation relates the mole fraction of monomers in the polymer to the composition of the feedstock via the reactivity ratios.

- Different classes of behavior may be assigned based on the product of the reactivity ratios...
- Statistical considerations give predictions for the average sequence length and sequence length distributions in a copolymer on the basis of reactivity ratios and feedstock composition.
- That's it for the last topic.
- Now it's onto step-growth polymerizations.
- Step-growth polymerizations: An introduction.
 - This is a review of the intro slides.
 - The invention of step polymerization is often credited to Wallace Hume Carothers and Julian Hill.
 - They prepared polyesters from propylene glycol and hexadecanedioic acid to make artificial silk fibers (1929 at DuPont).
 - Conclusions.
 - Difficult to produce high molecular weight polymers.
 - M_n initially limited to 1500-4000; acid catalyst increases M_n .
 - Equilibrium reaction; remove water to increase M_n to 12,000.
 - Conclude that...
 - "Atractive appearance" is a direct quote — old chemists were very descriptive!.
 - ...
 - From a JACS paper in 1929.
- Some commercial step-growth polymers.
 - Polyester, nylon, Kevlar, polyurethane, etc.
- Step-growth polymerization: Introduction.
 - Di-acids and di-amides.
 - In many step-growth reactions, a low-molecular weight byproduct (X) is produced.
 - Because the reactions are equilibriums, the byproduct must be removed to shift the equilibrium to the product side and create high-molecular weight products.
 - Since the byproduct is often removed by condensation (H_2O , MeOH , ...), the reaction is termed **polycondensation**.
 - Thus, for historical reasons, the terms step-growth polymerization and polycondensation are often used synonymously, although this is not always correct.
 - Important exception: Urethanes do not produce any condensation product.
- Step-growth polymerization: General mechanism.
 - Mechanism: Oligomers combine.
 - Rapid disappearance of monomer species.
 - Makes these harder to track by NMR.
 - Reactivity of functional groups is independent of chain length.
 - Molecular weight increases slowly.
 - No initiator (although catalyst can help kinetics).
 - This makes the kinetics a bit easier actually.
 - Chain ends are still active.
- Molecular weight.

- What is a polymer?
 - Controversial question.
 - Rowan says when you get above the entanglement rate.
- Practical consideration.
 - Only polymers with M_n of $> 10\,000\text{ g mol}^{-1}$ have useful mechanical properties.
 - Note: Electronic polymers may be useful at lower M_n .
- **Structural unit = monomer unit = residue**, e.g., a diol or diacid..
- **Repeat unit**: A segment of one or more structural units that repeats along the polymer chain.
- The **number-averaged ...**
- Number average degree of polymerization.
 - Can be simply defined as the total number of molecules originally present in the system N_0 divided by the total number of molecules in the system after the polymerization N .
 - If $[M]$ is the concentration of molecules, then

$$\overline{X}_n = \frac{N_0}{N} = \frac{[M]_0}{[M]}$$

- X_n can also be related to the concentration of one of the functional groups $[M]$ present after a fraction p has been reacted, where $[M]_0$ is the initial concentration of one of the functional group.
- A bit more stuff gets you back to **Carothers Equation**, proposed by Carothers in 1936.

$$\overline{X}_n = \frac{1}{1-p}$$

- This emphasizes the need for nearly quantitative chemistry once again (i.e., chemistry for which $p \rightarrow 1$).
 - Number-average molecular weight.
 - Defined as the total weight of a polymer sample divided by the total number of moles in it.
 - Given by
- $$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x} = M_0 \overline{X}_n + M_{\text{eg}} = \frac{M_0}{1-p} + M_{\text{eg}}$$
- It is important to note for type AA + BB polymerizations, the repeat units contain bits of both monomers. Therefore, M_0 is the **mean molecular weight** of the two structural units (see below)...
 - What is the impact of the Carothers equation?
 - Step-growth polymerization is challenging.
 - If your chemistry isn't perfect and your reaction isn't driving you to high conversions, it's not going to work.

- Molecular weight and stoichiometric.

- The reactant ratio r (*not to be confused* with the reactivity ratio; horrible choice of notation).
- For non-stoichiometric monomer ratios, the **reactant ratio** r is introduced.

$$r = \frac{N_A}{N_B}$$

- Note that $r \leq 1$.

- N_A, N_B are the numbers of functional groups A and B initially present.
 - The total number N_0 of molecules initially present becomes

$$N_0 = \frac{N_A + N_B}{2} = \dots$$
 - ...
 - We get to

$$\overline{X}_n = \frac{1 + r}{1 + r - 2rp}$$
 - Table.
 - Chart.
- Molecular weight control.
 - ...
 - Since in step polymerization, DP (degree of polymerization) is a function of reaction time, it can — in principle — be controlled by the latter (i.e., the reaction can be quenched once the desired molecular weight is obtained).
- Molecular weight and stoichiometric.
 - Case of an AA/BB polymerization.
 - Monomer BB is used in excess.
 - End cappers case.
 - ...
 - Here, we have

$$r = \frac{N_A}{N_B + 2N'_B}$$
 - Type 3: For an A–B monomer, the r is automatically 1.
- Molecular weight distribution.
 - Most probable dispersity is 2.
 - Breadth of molecular weight distribution.
 - We also have the weight-averaged degree of polymerization.
- General considerations on step-growth polymerization chemistry.
 - High degree of polymerization only at high conversions.
- Basic chemistry of carboxylic acid derivatives.
 - Functional group and type of polymer.
 - To polymerize these guys, all we need is OChem II.
 - We heat the monomers to 200 °C under vacuum and just drive off the water.
 - This is super easy to do at large scale.
 - This is why nylon is produced commercially: We can just heat it up really hot and in bulk batches.
 - Polycarbonates: Alcohol plus phosgene.
 - Polyurethanes: Alcohol plus isocyanate.
 - We can utilize all of these chemistries!

8.2 ???

2/22:

- Final is 3/5, 10-12 in this room.
- Last time, we started talking about chain-growth polymerizations. What do we remember?
 - You want your stoichiometry to be as close to one as possible.
 - We want things to be nearly quantitative.
 - Works well in large batch.
 - Sometimes we need a catalyst; initiators aren't needed, though.
 - We need to drive the polymerizations by removing the condensation product.
 - Most recyclable commercial plastic right now is PET (polyethylenetethalate).
 - We can *chemically* recycle this since it has an ester backbone. (vs. *mechanical* recycling)
 - This is fairly new...
- Basic chemistry of carboxylic acid derivatives.
 - This mechanism is similar for polyester, polyamide, polyimide, etc.
 - An acid-catalyzed process adds an acid to the carbonyl. This makes the carbon even more electrophilic. We get to the tetrahedral intermediate, and then electrons kick down and kick out hydroxide/water.
 - Every step is completely reversible and we have to account for this when we think about the kinetics.
 - Removing the water uses Le Châtelier's Principle to drive the equilibrium to the right.
 - The rate-limiting step is the alcohol/amine reacting with the activated acid (k_3).
- Kinetics of the polyesterification of diacid and diol.
 - Equal reactivity of the functional groups on each end of the monomer.
 - The reactivity of the FGs is largely independent of chain length.
 - Reaction state can be monitored by looking at how many intact end groups you have left.
 - The rate of reaction is expressed in terms of the concentrations of the reacting FGs.
 - The rate of polyesterification:

$$R_p = -\frac{d[\text{R-COOH}]}{dt} = \dots$$

– ...

– $[\text{R-C}(\text{OH})_2^+]$ is difficult to measure. However,

$$K = \frac{[\text{R-C}(\text{OH})_2^+]}{[\text{R-COOH}][\text{HA}]}$$

– Therefore,

$$R_p = \dots$$

– Now we can also have a self-catalyzed polymerization.

■ In the absence of additional strong acid, R-COOH assumes the role of HA .

– Thus, here,

$$R_p = -\frac{d[\text{R-COOH}]}{dt} = k[\text{R-COOH}]^2[\text{R-OH}]$$

■ The experimentally determined rate constant k in this equation equals Kk_3 .

■ This is a third-order reaction.

- ...
- In terms of the **extent** or **fraction of conversion**

$$p = \frac{[M]_0 - [M]}{[M]_0}$$

we have that

$$2kt = \frac{1}{[M]^2} - \frac{1}{[M]_0^2}$$

...

- Accessibility of functional groups.
 - To yield a high-MW polymer, the polymer must not precipitate from the polymerization mixture before the desired molecular weight is reached.
 - Often tricky due to the limited choice of solvents that dissolve the polymer and are compatible with the reaction conditions.
 - In xylene, the polymer precipitates at once.
 - In nitrobenzene, the polymer precipitates after 30 min.
 - In DMSO, the polymer is directly soluble.
- Equilibrium considerations.
 - Most step polymerizations involve equilibrium reactions. Thus, it is important to elucidate how the equilibrium affects the extent of conversion. Compare closed system with open system.
- Equilibrium conditions (closed).
 - The polymer and condensation products build up until the rate of the reverse reaction (depolymerization) equals that of the forward.
 - The equilibrium constant equals

$$K = \frac{p^2}{(1-p)^2}$$

- It follows that

$$p = \frac{\sqrt{K}}{1 + \sqrt{K}}$$

- This tells you that your equilibrium constant basically has to be in the hundreds of thousands or millions to get anything resembling polymer.
- Esterification equilibrium constant is somewhere between 1 and 10, so it definitely has to be driven.
 - Amides are 100-1000.
 - In a closed system, you'll never defeat the laws of thermodynamics.
- We get

$$\overline{X}_n = 1 + K^{1/2}$$

- Equilibrium conditions (open).
 - High MWT polymers require an open, driven system: At least one of the products of the forward reaction must be removed to drive the equilibrium towards high molecular weights.
 - Remove volatile, low-molecular weight byproducts such as water, methanol, etc. with temperature, reduced pressure, and purging with an inert gas (e.g., nitrogen or argon).
 - HCl can be removed by adding a base to neutralize the acid once created.

- Sometimes the product is eliminated from the reaction because it precipitates.
- You can get diffusion control as viscosity skyrockets; this is how you get bubbles in your polymer.
- We get

$$\bar{X}_n = \left(\frac{K[M]_0}{[H_2O]} \right)^{1/2}$$

- Thus, even with a crappy K , we can get high molecular weight with water removal.
 - We don't need to remove all of the water.
 - There are engineering approaches to removing water and preventing bubbles, such as thing sheets and curing, running the system in an emulsion to aid SA:Volume ratio, etc. It doesn't all have to be in a big vat!
- Polymerization vs. cyclization.
 - A polymer can react intramolecularly and close up into a ring.
 - In most any chain-growth polymerization, you will get some competitive ring formation.
 - You do have to pay an entropy penalty to bring the two chain ends close together, but it will still happen in some equilibrium.
 - Ring formation is usually undesired.
 - Whether for a particular system ring-formation is competitive with linear polymerization depends on both thermodynamics and kinetic considerations.
 - We don't often form small rings; if you're designing a polymerization and you know that six-membered rings could form, that's not one you'd choose to run because you'll just be fighting against that the entire time.
 - Kinetics of cyclization.
 - Kinetic feasibility.
 - The kinetic feasibility of ring formation depends on the probability of two groups of the reactant molecule to approach each other to react.
 - As the potential ring size increases, the molecule...
 - Kinetic feasibility decreases with ring size.
 - You need a good solvent that swells the chain and makes it stretch out rather than bunch.
 - Tendency of cyclization.
 - The easiest ring to form kinetically is three. It's terrible thermodynamically, but it's kinetically great.
 - Thus, we've got a balance.
 - The effect of cyclization is also counterbalanced by the concentration factor; high concentration = fewer cycles; low concentration = more cycles.
 - Many commercial processes remove low molecular cyclics by extraction or devolatilization or boiling them off at really high temperatures.
 - Early in the chart, it's kinetically feasible.
 - Later on, ring strain is no longer a problem and we're entirely in the realm of kinetics.
 - Interchange reactions.
 - Some polymers (polyesters, polyamides, etc.) can — under appropriate conditions...
 - Step-growth copolymers.

- Homopolymers are easy.
- Copolymers; we can get different values for the numbers of polymers.
- Alternating copolymers vs. statistical and random copolymers.
- Step-growth copolymer synthesis.
 - Overall copolymer composition is usually the same as the feed ratio as the reaction will need to be taken to 100%.
 - Random copolymers are common as usually the reactivity of the functional groups in the different monomers of the same size.
- So that's all the chemistry.
- Now, we'll talk about some specific polymers.
- PET.
 - Poly(ethylene terephthalate).
 - Anything that says polyethylene on our clothes.
 - Coke bottles.
 - The most important commercial polymer.
 - Aka Mylar, Dacron, Terylene.
 - Melting point at 255 °C.
 - Glassy transition temperature at 80 °C.
 - Optically clear.
 - Potentially high crystallinity.
 - High density.
 - Cheap.
 - Good mechanical properties.
 - Good chemical resistance (labile in strong acids and bases).
 - Low dye-ability.
 - Fibers.
 - $M_n > 15\,000$.
 - Melt-spinning, etc.
 - Use in apparel, curtains, upholstery, fishing lines, ...
 - Films.
 - Use in: Audio and video tapes, floppy disks, capacitors.
 - Bottles.
 - $M_n > 25\,000$.
 - Solid-state post condensation.
 - Low crystallinity pre-form; stretch blow molding.
 - *These* are not the ones that leach into water; it's the polycarbonates, such as BPA.
- PET synthesis.
 - Ester-interchange route.
 - First stage.
 - A mixture of dimethyl terephthalate and excess ethylene glycol (as solvent) are heated. Methanol is released as a vapor.

- Second stage.
 - Much hotter, lower pressure. Ethylene glycol comes off now and the polymer grows.
- Second step.
 - Antimony (Sb) centered polycondensation catalyst.
 - This catalyst is the reason we can get clear Sprite bottles now.
 - The reason we used to have green Sprite bottles is that the PET would be yellow with the old catalyst and then they would add a blue dye because no one wants to be drinking out of a pee-colored bottle.
 - Then the chemistry evolved and now we can make clear bottles.
- Polyester side reactions.
 - Ethylene glycol can self-react, releasing water, to form di-ethylene glycol.
 - We can also get dehydration.
 - The reason that polymers start to get brown at higher temperatures is that there's some degradation reactions forming UV chromophores; pure, it should be clear, white, or colorless.
- Other polyesters.
 - PETG.
 - Aliphatic polyesters.
 - Not usually as useful.
 - Used as plasticizers for PVC.
 - Diols can be used as building blocks for polyurethane.
 - Poly(lactic acid) is the only commercial scale polymer made from biological sources.
 - Liquid crystalline polymers...
- We'll start next class with BPA.

Week 9

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9.1 ???

- 2/27:
- Bisphenol A Polycarbonate.
 - Good optical properties (clarity).
 - When you microwave baby bottles with it, though, you get leaching.
 - Polycarbonate synthesis.
 - Interfacial polycondensation.
 - Rapidly stirred mixture of solvent (e.g., DCM, PhCl, DCE), aqueous NaOH, bisphenol A, phosgene, a tertiary amine catalyst, and a monofunctional end-capper for MW control.
 - IN the aqueous phase, there are some reactions. In the organic, there are others. At the interface, there are still more.
 - You can also do transesterification.
 - Melt of Bisphenol A, diphenylcarbonate, sodium bisphenolate catalyst.
 - High temperature and low pressure.
 - You get some undesired side reactions.
 - Polyamides (nylons).
 - Linear aliphatic polyamides will be our focus.
 - The first one was “Polyamide x,” aka Perlon™.
 - “Polyamide x,y” was Nylon™.
 - Polyamides History.
 - Kirby and Carothers (1930) failed to polymerize caprolactam, and put this result in writing in JACS stating that it couldn’t be done. German IG Farben was then able to do it and patent it.
 - ...
 - Peterson in Carothers’ lab made polyamide 5-10 with even better characteristics.
 - Triggered by the business people at DuPont, who were concerned that polyamide 5-10 was too expensive to make, Carothers’ group started to screen...
 - 1935: Berchert prepared the first sample of polyamide 6,6. The polymer had exciting properties (although the high melt temperature suggested possible problems due to degradation upon processing) and the economics of the monomers were right, so that in summer 1935, polyamide 6,6 was selected as the commercial candidate.
 - The “solidification” was a cold crystallization.

- 1939: Polymer brought to market.
- Polyamide.
 - List of properties.
 - Moderate to high crystallinity.
 - High water uptake (wet nylon is softer).
 - The keratin in our nails is polyamide, too, with some side groups. Thus, it has high water uptake, too. That's why our nails get soft in the bath!
 - Few solvents: Hexafluoro-2-propanol, formic acid, *m*-cresol.
 - ...
- Application of polyamides.
- Polyamide fibers.
 - We get a lot of hydrogen bonding that stops chains from slipping past each other.
 - Hydrogen bonding is stronger than the dipole interactions in polyesters (use in gen-chem review??), creating ordered crystalline polymer chains.
- Polyamide 6,6 synthesis.
 - The nylon rope trick, forming nylon via interfacial polymerization.
 - If the rate of reaction is faster than the rate of pulling up the polymer, you'll get a nice long rope.
 - Melt polycondensation.
 - Steps to do it.
- Polyurethanes.
 - Very easy to make.
 - You can do the reverse reaction with catalysts above 180 °C.
 - Most polymerization is done with a catalyst under 100 °C, though.
 - These can be made as either fibers or foams.
 - Lists a number of possible di(isocyanates) and diols.
 - There are literally thousands of polyurethanes.
 - Some are very stiff, e.g., polyurethanes are used in bowling balls.
 - Some are very soft and stretchy, e.g., spandex and shower curtains.
 - Polyester leisure suits in the '70s, spandex in the '80s. As a polymer chemist, with great power comes great (fashion) responsibility.
- Polyurethane fibers.
 - Commercially, the most important polyurethane fibers are those that result in a blocky copolymer structure (e.g., spandex).
 - To make these, a low molecular weight polymeric diol ($M_n = 2000 - 3000$) is reacted with excess isocyanate to result in isocyanate-terminated polymer which is then reacted with a diamine chain extender.
- Polyurethane foams.
 - ...
- Aromatic polymers.

- Polysulfone (PSU) is a rigid, high-strength, semi-tough thermoplastic that has a **heat deflection temperature** of 174 °C and maintains its properties over a wide temperature range.
 - Synthesized via a nucleophilic substitution-type mechanism.
- Polyetheretherketone (PEEK).
- EWGs to pull electrons up before they kick back down are critical in the synthesis for both of these.
- Poly(imide).
 - Really good strong materials.
 - Nucleophilic aromatic substitution mechanism here, too.
 - You go through a **polyamic acid** intermediate. This is solution processible. Then when you “heat the bajesus out of it,” you form the polyimide.
- Poly(ether imide).
 - Same NAS mechanism.
- Poly(phenylene oxide).
- Poly(phenylene sulfide).
- **Heat deflection temperature:** The temperature at which a polymer starts to “soften” under a fixed load.
- Reminder: Most polymer chemistry is done under extreme conditions that we wouldn’t ordinarily find in the lab.
 - We often try to use more mild conditions when we have more functional groups, as in polyurethanes, though.
- Branched and network polymers.
 - We’ll start this today, finish it on Thursday, and then half the class will be left. Rowan is open to any activity we want to propose. He can go over anything again, etc.
- Reactions with monomers with more than two functional groups.
 - All the step-growth polymerizations so far have focused on monomers with only two reactive groups which lead to the formation of either linear polymers or rings.
 - Consider the polymerization of A–B monomer in the presence of a small amount of A... **functionality**
- Crosslinking.
 - Reacting A–B with A_f in the presence of B–B leads to branching and crosslinking.
 - Crosslinking also occurs with

$$A-B + B_f \longrightarrow A-A + B-B + B_f \longrightarrow A_f + B_f \longrightarrow$$
 - Crosslinking is distinguished by the occurrence of **gelation** during the polymerization.
 - At this gel point, an insoluble polymer fraction (**gel**) is formed.
 - It’s all just one big ass molecule.
- Networks: Definitions.
- **Junction:** Point where three or more strands emanate.
- **Functionality** (of a junction): The number of strands connected to it. *Denoted by f.*
- **Strand:** A polymer chain that bridges two junctions.

- **Loop:** A network defect that begins and ends at the same junction point and is not fully elastically active.
- **Dangling chain end:** A network defect that is free to relax and as such does not contribute to the network elasticity.
- Loops and dangling chain ends are *defects*.
- **Sol fraction:** This is the fraction of polymer that is not part of the infinite network either as a linear polymer or as part of a cluster.
 - If put in a good solvent, the sol fraction would dissolve and the **gel fraction** would not.
 - After you synthesize your polymer, you identify the gel fraction by washing it, drying it, and weighing it.
- **Networks:** A class of polymers that consists of an infinite crosslinked architecture.
 - The linkages prevent flow of the material, and as such, these materials are solids.
 - Two main classes of networks: **elastomers** and **thermosets**.
- **Elastomer:** ...
- **Thermoset:** ...
- **Gel point:** The point during the polymerization at which gelation occurs.
 - A key property of crosslinked polymers is that they never dissolve. They may swell, but they will never dissolve unless we break bonds.
 - Definition of the **sol**.
 - Once the gel point is reached, the polymer will no longer flow (even at high temperatures). Thus, processing needs to be completed before gelation sets in.
 - Thus, the **prepolymer** is processed before gelation is reached, and polymerization/crosslinking is completed after processing.
 - Three stages for thermosetting polymers or thermosets.
 1. Polymer soluble and fusible.
 2. Polymer still fusible but close to the gel point.
 3. Polymer highly crosslinked...
- **Sol:** Any non-gel portion of the polymer which remains soluble.
- Network synthesis.
 - It is important to understand the relationship between extent of reaction and gelation. This can be done based on calculating when either \bar{X}_n and \bar{X}_w reach an infinite size.
 - Carothers equation: $\bar{X}_n \rightarrow \infty$.
 - You have to think about the stoichiometric amount of reagents.
 - This is based on the average functionality of the monomer mixture, i.e., the average number of functional groups per monomer molecule:

$$f_{\text{avg}} = \frac{\sum N_i f_i}{\sum N_i}$$

- Recall that N_i is the number of molecules of monomer i with functionality f_i .
- Example: For 2 mol of glycerol (triol) and 3 mol of phthalic acid (diacid), then

$$f_{\text{avg}} = \frac{12}{5} = 2.4$$

- For the system where the number of A and B groups are equal, the number of monomers...
- ...
- Combining equations, we get

$$\overline{X}_n = \frac{2}{2 - pf_{\text{avg}}}$$

- Rearranging, we obtain

$$p = \frac{2}{f_{\text{avg}}} - \frac{2}{\overline{X}_n f_{\text{avg}}}$$

- This relates the extent of reaction and degree of polymerization to the average functionality in the system.
- The gel point is where $\overline{X}_n = \infty$. Thus, the **critical extent of the reaction** p_c when gelation occurs is

$$p_c = \frac{2}{f_{\text{avg}}}$$

- ...
- When the two functional groups are not at stoichiometry, then the average functionality of the molecules is twice that of the amount of the functional group not in excess divided by the number of molecules, i.e., the extent of crosslinking (if it occurs) depends on the deficient functionality.
- Example: *picture of glycerol and phthalic acid*.
 - ...
- Extension to nonstoichiometric reactant mixtures.
- The average functionality of a system containing more than two monomers can be calculated in a similar manner.
- Consider a three component system...
- Experimental gel points.
 - The Carothers (and statistical theoretical approaches not covered here) differ in their predictions of extent of reaction, p_c .
 - The gel point is usually determined experimentally as the point in the reaction at which the mixture loses fluidity (as indicated by the failure of bubbles to rise).
 - The data shows that gelation usually happens a bit before the Carothers prediction and after the statistical prediction.
 - ...

9.2 ???

- 2/29: • I was at KHS Immersion Weekend.