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", IPUAC 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.

  - **Carotherts 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 agin.

- 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 standars.

    - ■ 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 molecula 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.
  $$OCN-R-NCO + HO-R'-OH \longrightarrow Polyurethane$$
  - Why distinguish between chain-growth and step-growth?
    - The mechanisms and setups are quite different.

- Chain (addition) polymerizations. *picture*

  - R^* + Monomer $\longrightarrow$ $R-M^*$
  - And then repeat.
  - So a few initiatiors 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 to 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. $585\,\text{kJ/mol}$ to 2 σ-bonds (2x ca. $330\,\text{kJ/mol}$)).
  - The overall polymerization generallly involves 4 basic reactions: Initiation, propagation, termination, and chain transfer.

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

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 questions 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 densituy from the π-bond is withdrawn by the carbonyl into the ester. Most substituents that have a multiple bond adjacent to the doulbe 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 activiating 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 additio 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 additio 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 conditinos, 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 $200\,^\circ$C.

- Comparision 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 ggeneral types: Isotactic, syndiontactic, 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...