Week 8

???

8.1 ???

- 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_1r_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 equtions 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 prouduced.
  - – 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 synonomously, althoughthis 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 polyners with M_n of $> 10\,000\,\mathrm{g\,mol^{-1}}$ 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

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

  - 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 $[\mathrm{M}]_0$ 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 $p \to 1$).

- Number-average molecular weight.
  - Defined as the total weight of a polymer sample divided by the total number of moles in it.
  - Given by
  $$\overline{M}_n = \frac{\sum N_x M_x}{\sum N_x} = M_0 \overline{X}_n + M_{\mathrm{eg}} = \frac{M_0}{1 - p} + M_{\mathrm{eg}}$$
  - 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.

  $$r = \frac{N_\mathrm{A}}{N_\mathrm{B}}$$

    - 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

$$N_0 = \frac{N_A + N_B}{2} = ...$$

– ...

– 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 (poly$\underline{e}$thylene$\underline{t}$ethalate).
        - 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 electrophylic. 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:
$$R_p = -\frac{\mathrm{d[R-COOH]}}{\mathrm{d}t} = ...$$
    - ...
    - $[\mathrm{R-C(OH)_2}^+]$ is difficult to measure. However,
$$K = \frac{[\mathrm{R-C(OH)_2}^+]}{[\mathrm{R-COOH}][\mathrm{HA}]}$$
    - Therefore,
$$R_p = ...$$
    - Now we can also have a self-catalyzed polymerization.
        - In the absence of additional strong acid, $\mathrm{R-COOH}$ assumes the role of HA.
    - Thus, here,
$$R_p = -\frac{\mathrm{d[R-COOH]}}{\mathrm{d}t} = k[\mathrm{R-COOH}]^2[\mathrm{R-OH}]$$
        - 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 precipitats 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 viscocity skyrockets; this is how you get bubbles in your polymer.
  - – We get

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

  - – 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 lienar 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 estraction or devolatization 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.
  - Alternatign 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, curtians, 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 synthsis.

  - 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.