

# Week 4

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## 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.
      - $\text{Cl}^-$  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.,  $-70^{\circ}\text{C}$  or even  $-80^{\circ}\text{C}$ .
    - 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  $\sigma$ -bonded electrons rather than unshared/nonbonding- or  $\pi$ -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: ...
    - ...
    - Aluminum<sup>1</sup>:  $2 \text{AlBr}_3 \rightleftharpoons \text{AlBr}_2^+ + \text{AlBr}_4^-$ .
      - Notice all the “big, hairy counterions.”
  2. Cationation.
    - ...
- I. A. Brønsted (protic) acids.
  - We generate  $\text{H}^+$  ions, and then the first  $\text{H}^+$  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.
    - $\text{AlCl}_3$ ,  $\text{BF}_3$ ,  $\text{SnCl}_4$ , ...
  - There are organometallic derivatives.
    - These are more soluble in the organic solvents we use, and hence better for that reason.
    - Examples:  $\text{RAlCl}_2$ ,  $\text{R}_2\text{AlCl}$ ,  $\text{R}_3\text{Al}$ .
  - 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  $\text{AlEt}_3$ , then we can generate  $\text{H}^+$  and  $\text{AlEt}_3\text{OH}^-$ .
  - 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.

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<sup>1</sup>Historically, 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:  $\beta$ -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  $\pi$ -bonds to  $\sigma$ -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  $-100^\circ\text{C}$ , 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 ( $\text{H}^-$ ) and methide ( $\text{CH}_3^-$ ) 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  $\beta$ -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  $\beta$ -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/I<sub>2</sub>.
    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.,  $\text{ZnX}_2$ ) 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; Me<sub>6</sub>TREN is 10,000 times more active than Et<sub>6</sub>TREN.