

# 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  $\alpha$ -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  $\alpha$ -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 ( $\text{AlEt}_3$ ) to initiate the reaction.
  - Present-day *super-active* or *high-mileage* system: A heterogeneous catalyst.
    - Ball milling...
  - With  $\text{MgCl}_2$  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  $\alpha$ -olefins work, but basically anything else doesn't.
- Potential solution:  $\alpha$ -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  $\beta$ -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)<sup>1</sup>.
  - This is a condensation polymerization.

---

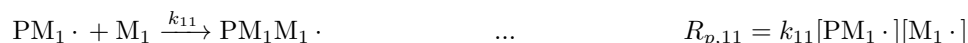
<sup>1</sup>Sounds like Anderson misnamed this!

## 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  $\text{M}_2$ .
  - If  $r_1 > 1$ , then  $\text{PM}_1 \cdot$  preferentially adds to  $\text{M}_1$
  - 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  $\text{M}_1$  in the polymer.
    - This means that  $F_1 + F_2 = 1$ .
  - $f_1$  is the mole fraction of  $\text{M}_1$  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  $\text{M}_1$  and  $\text{M}_2$  sequences, the **sequence length distribution**.
  - The mole fractions of  $(N_1)_x$  and  $(N_2)_x$  of forming  $\text{M}_1$  and  $\text{M}_2$  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  $\text{M}_2$ 's will be by themselves and there will be a more stretched out exponential distribution of  $\text{M}_1$ .
    - In cases where both are small, both  $\text{M}_1$  and  $\text{M}_2$  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.