Unit 5

???

5.1 Lecture 18: Olefin Polymerization

5/10:

- Another huge industrial-scale reaction
- The Great Pacific Garbage Patch is largely composed of plastics made by this process.
  - Plastics get a bad rep, but they are a remarkable material.
    - We can melt them, form them, and they have durability properties.
  - However, because of their environmental impact, a big thing in chemistry is the pursuit of materials with similar properties that are biodegradable.
  - Inorganic chemistry plays a large role in their synthesis.
  - In 2008, the US alone made 58.3 million metric tons of polyethylene and 17 million metric tons of polypropylene.
- General form:

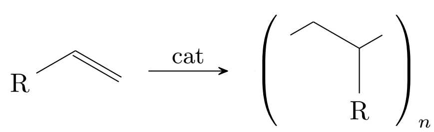


Figure 5.1: The general form of olefin polymerization.

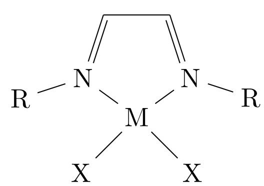
  - If R = H, we have polyethylene.
  - If R = Me, we have polypropylene.
- This is a thermodynamically favorable, exothermic reaction since π bonds are weaker than σ bonds.
- The catalyst is typically Ti, Zr, Hf, Cr (early Group 4 transition metals). Sometimes we use Fe, Co, Ni, and Pd (these are a bit more specific).
- Most of the materials that mediate this catalysis are called Ziegler-Natta catalysts.
  - These are heterogeneous, even though they operate via the same kind of catalytic cycle that homogeneous systems use.
  - Nobel prize (1963).
- Polymer terms:
- **Number averaged molecular weight**: The quantity $\frac{\sum N_xM_x}{\sum N_x}$, where N_x is the number of chains with molecular weight x and M_x is ?. *Also known as* $\boldsymbol{M_N}$.

- **Weight averaged molecular weight**: The quantity $\frac{\sum N_x M_x^2}{\sum N_x M_x}$. *Also known as* $\boldsymbol{M_w}$.
- **Molecular weight distribution**: The quantity $\frac{M_w}{M_N}$. *Also known as* **polydispersity index**, **PDI**.
  - 1 is perfect. This means that you only have one type of chain.
  - 1.1 is good.
  - Above 1.5 is getting ill-defined.
- Stereochemistry:
  - Normally, the methyl groups in polypropylene all insert on the same side, but if one misinserts, then it faces the other direction.
  - If the catalyst corrects itself and continues on inserting in the original direction, this is **site control**.
- **Site control**: The catalyst controls the insertion.
  - More specifically, the direction the methyl groups point is controlled by the catalyst.
- **Chain end control**: One misinsertion causes the ensuing insertions to face the same way as the last inserted methyl group.
  - More specifically, the direction the methyl groups point is controlled by the last inserted methyl group.
- Mechanism:

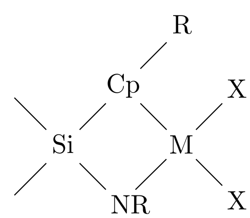
$$\mathrm{L}_n\mathrm{MR}_2 \xrightarrow[-\mathrm{LAR}^-]{\mathrm{LA}} \mathrm{L}_n\mathrm{MR}^+ \xrightarrow{||} \mathrm{L}_n\mathrm{M}\text{---}\mathrm{R} \longrightarrow \mathrm{L}_n\mathrm{M{-}H}$$

  - The three steps are activation, growth, and termination.
  - LA stands for Lewis acid. The lewis acid activates the catalyst by abstracting an anionic Lewis acid species.
  - Olefin insertion grows the polymer.
  - β-H elimination is the simplest way to terminate the chain, even though there are several possibilities.
- Activation:
  - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR_3/MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{AlR_4}^-]{\mathrm{AlR_3/MAO}} \mathrm{L}_n\mathrm{Me}^+$.
  - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR_3/MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{MeBAr^F}_4{-}]{\mathrm{BAr^F}_3} \mathrm{L}_n\mathrm{Me}^+$.
  - $\mathrm{L}_n\mathrm{MCl}_2 \xrightarrow{\mathrm{AlR_3/MAO}} \mathrm{L}_n\mathrm{MMe}_2 \xrightarrow[-\mathrm{CH_4}]{\mathrm{HBAr^F}_4} \mathrm{L}_n\mathrm{Me}^+$.
  - MAO is methylated aluminum oxide.
    - An ill defined, amorphous gunk with some oxygens created by adding a pinch of water to $\mathrm{AlMe_3}$.
    - A cheap reagent that people chuck into their catalyst mixture.
    - Functions:
      1. Alkylating agent.
      2. Activator (pulls off methyls to generate cationic species).
      3. Scavenger for water (primarily) and oxygen.
  - The fluorinated aryl borates are really good because they're very weakly coordinating, and we really want an open coordination site.

- Chain growth:
  - $MR(||) \longrightarrow M{-}{-}{-}R \xrightarrow{||} M(||)({-}{-}{-}R) \longrightarrow M{-}{-}{-}R \longrightarrow \ \longrightarrow \ \longrightarrow .$
  - This is called the Cossee Arlman mechanism.
  - Sterics determine the rates: Ethylene > propylene > substituted olefins > disubstituted olefins ≈ geminal disubstituted olefins >>> trisubstituted or tetrasubstituted olefins.
- Termination:
  - How you get variability in chain lengths.
  - Control it by adding a chain-transfer reagent (a specific terminating reagent). Examples include...
    - H_2: $L_nM{-}pl \xrightarrow{H_2} L_nM{-}H + H{-}pl$, where pl is a polymer[1].
    - β-H elimination: $L_nM{-}{-}{-}pl \longrightarrow L_nM(H)(||pl) \longrightarrow L_nM{-}H + ={-}pl$.
    - β-H abstraction: $M(||)({-}{-}{-}pl) \longrightarrow M(Et)(||pl) \longrightarrow MEt + ={-}pl$.
- The relative rates of growth vs. determination dictate the type of material we get.
  - K_p is the rate of growth/propogation; K_t is the rate of termination.
  - K_p vs. K_t dictates the product.
  - $K_p >>> K_t$ yields high molecular weight polymers.
  - $K_p \approx K_t$ (within the same order of magnitude) yields oligomers.
    - The geometric weight distribution of oligomers is called a **Schultz-Flory distribution**.
  - $K_t >> K_p$ yields dimers exclusively.
    - This can be valuable if you just want to transform ethylene into butadiene (a higher value product), for instance.
- Types of polyethylene.



(a) LDPE catalysts.



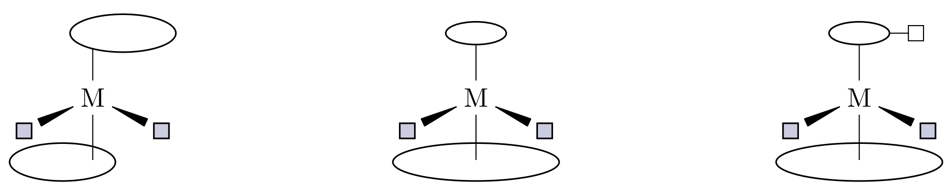
(b) LLDPE catalysts.

Figure 5.2: Polyethylene-type catalysts.

- A perfect zig-zag chain is HDPE (high density polyethylene).
  - High melting point.
  - Crystalline.
  - Example uses: Helmets for army soldiers, bulletproof plastics.
  - Usually formed with Ziegler-Natta catalysis:
    - $TiCl_x + AlR_x \longrightarrow$ a heterogeneous catalyst that's super active ($> 10^9$ kg of polymer per gram of catalyst).
    - Note that $x = 3$ or 4.
    - Alternate catalysts: $Cr^{III} + \text{silica} \xrightarrow{O_2,\Delta} CrO_4 \xrightarrow{||}$ reduced Cr center (the active catalyst).

[1] Be aware that Anderson uses a capital P in a circle.

- A mess with a ton of branching is LDPE (low density polyethylene).
  - Lower melting point.
  - Often made by radical processes.
  - Also made by late transition metal catalysts, where there's less control over chain growth:
    - Square planar, d^8, $16\,\mathrm{e}^-$ species.
    - Example metal centers: Ni, Pd.
    - High rates of β-H elimination leads to chain walking and branching.
- Longer chain with a few branches is linear low-density polyethylene (LLDPE).
  - Transition metal catalyzed.
  - Formed from a mixture of ethylene and substituted olefins or a controlled rate of branching from catalysts.
  - Catalysts:
    - Constrained geometry catalysts.
    - Example metal centers: Ti, Zr, Hf.
- Polyethylene gives a single chain, but polypropylene can be chiral depending on the orientation of the methyl groups. The orientation defines **tacticity**.
- **Isotactic** (polypropylene): All methyl groups are pointed in the same direction.
  - The most crystaline, highest melting point material.
- **Atactic** (polypropylene): Every methyl group is random.
  - The least crystaline, lowest melting point material.
- **Syndiotactic** (polypropylene): Every methyl group alternates.
  - Pretty highly ordered.
- **Hemiisotactic** (polypropylene): Every other methyl group points the same direction; the remaining ones are random.
- **Stereoblock** (polypropylene): Alternating blocks of isotactic polypropylene.
- Controlling stereochemistry:
  - Relies on the fact that propylene is pro-chiral.
  - Si (pro-S) and Re (pro-R) faces.
  - Catalyst symmetry controls tacticity.
- Catalyst types:



(a) C_2 symmetry. (b) C_s symmetry. (c) C_1 symmetry.

Figure 5.3: Polypropylene-type catalysts.

- Most well worked out for metallocenes.
- In Figure 5.3, boxes are open coordination sites; circles are space-filling ligands.
- Differences help dictate tacticity.
- C_2: Both binding sites are the same.
  - Steric clashing forces the olefin to point in inverted ways; but because the polymer switches sides, this leads to consistency in the direction the methyl is added.
  - Generates isotactic polypropylene.
  - Si-face selective.
  - Example: A diindene metallocene.
- C_s: Binding sites are enantiomers.
  - Generates syndiotactic polypropylene.
  - Two enantiotopic sites will alternate.
  - Example: A metallocene with Cp on top and fluorene on bottom.
- C_1: Binding sites are diastereomers.
  - Generates hemiisotactic polypropylene.
  - Example: A metallocene with Cp−R on top and fluorene on bottom.

- To make this work, the Cp rings are often tethered to prevent rotation.
  - However, rotation can be harnessed to make stereoblock copolymers.
- Note that stereoblock copolymers can also be synthesized with two isotactic catalysts, relying on chain transfer.
- Late-metals: Chain walking.
  - A chain can grow or it can chain walk (do β-H elimination followed by a $2,1$-insertion).
  - If it chain walks, we'll create a branch.
- We see this with late metals.
  - Early metals are terrible backbonders, so they will prefer to be on the alkyl side of the equilibrium.
  - Late metals can backbond, and will more readily form an olefin adduct (a necessary intermediate to chain walking).
- Thus, we use late metals...
  - Because sometimes we want branching, specifically finely tuned branching to a certain degree.
    - Recall that random branching can be achieved via a radical mechanism.
  - SHOP process:
    - We react ethylene with a nickel PO-type catalyst (a nickel catalyst with a bidentate ligand that chelates through a phosphorous and an oxygen), an enolate, or related phosphorous/oxygen based donors.
    - This creates olefin-terminating oligomers. This doesn't use chain walking, but rather the chain transfer process, which is much faster with late metals.
    - Products: C_4-C_8 (41%), C_{10}-C_{18} (40.5%), and C_{20+} (18.5%).
    - The short ones and the long ones can be combined with Mo_2O_3/Al_2O_3 to do olefin metathesis, yielding internal and terminal olefins.
    - Then, throwing in the medium-length ones and treating with $HCo(CO)_4$ (our hydroformylation catalyst) and syn gas yields terminal aldehydes, which with enough hydrogen can give us terminal alcohols, which are commodity chemicals.

- Oligomerization mechanism:

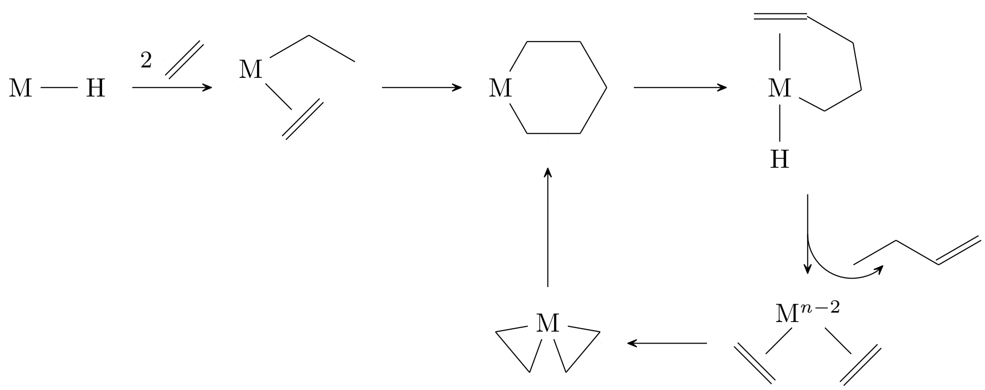


Figure 5.4: Oligomerization mechanism.

  - A metathesis-like process.
  - Example with nickel.

- Polar monomer incorporation.
  - One of the standing grand challenges in olefin polymerization.
  - Incorporating vinyl chlorides, vinyl ethers, vinyl esters, vinyl nitriles, etc.
  - We can do this with radical polymerizations, but there's no stereocontrol here.
  - PVC (pipe) is polyvinylchloride (robust, a great material, but opaque).
    - It's melting point would be even higher if we could make it isotactic (and it would be clear, which could potentially have applications).
  - The challenge with early metals is that if you β-Cl eliminate, the M−Cl bond will be too strong to break and reinsert the chloride. This kills the catalysis.
    - Additionally, the groups on the polymer adjacent to the metal center can donate to it, making the polymer a kind of chelating ligand and preventing olefin insertion. This also kills the catalysis.
  - Late metals are less halo/oxo-philic, which makes them better at incorporating these monomers.