Unit 5

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5.1 Lecture 18: Olefin Polymerization

- 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.
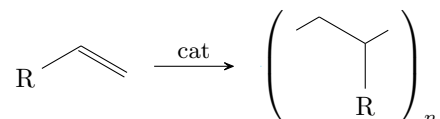
- General form:

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 $\frac{\sum N_x M_x}{\sum N_x}$, 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:

$$L_n MR_2 \xrightarrow[-LAR^-]{LA} L_n MR^+ \xrightarrow{\|} L_n M{-}{-}{-}R \longrightarrow L_n M{-}H$$
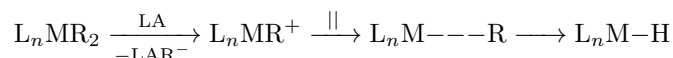
  - The three steps are activation, growth, and termination.
  - LA stands for Lewis acid. The lewis acid activates the catalyst by abstracting an anionic Lewis acid species.
  - Olefin insertion grows the polymer.
  - β-H elimination is the simplest way to terminate the chain, even though there are several possibilities.

- Activation:

  - $L_n MCl_2 \xrightarrow{AlR_3/MAO} L_n MMe_2 \xrightarrow[-AlR_4^-]{AlR_3/MAO} L_n Me^+$.

  - $L_n MCl_2 \xrightarrow{AlR_3/MAO} L_n MMe_2 \xrightarrow[-MeBAr^F_4{}^-]{BAr^F{}_3} L_n Me^+$.

  - $L_n MCl_2 \xrightarrow{AlR_3/MAO} L_n MMe_2 \xrightarrow[-CH_4]{HBAr^F{}_4} L_n Me^+$.

  - MAO is methylated aluminum oxide.

    - An ill defined, amorphous gunk with some oxygens created by adding a pinch of water to $AlMe_3$.
    - 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 $\approx$ 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: $L_n M{-}pl \xrightarrow{H_2} L_n M{-}H + H{-}pl$, where pl is a polymer[1].
    - β-H elimination: $L_n M{-}{-}{-}pl \longrightarrow L_n M(H)(||pl) \longrightarrow L_n M{-}H + {=}{-}pl.$
    - 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.
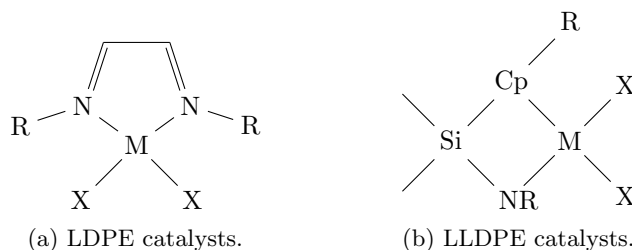

(a) LDPE catalysts.　(b) LLDPE catalysts.

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: $Cr^{III} + silica \xrightarrow{O_2, \Delta} CrO_4 \xrightarrow{||}$ reduced Cr center (the active catalyst).

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[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, $16\,e^-$ 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:

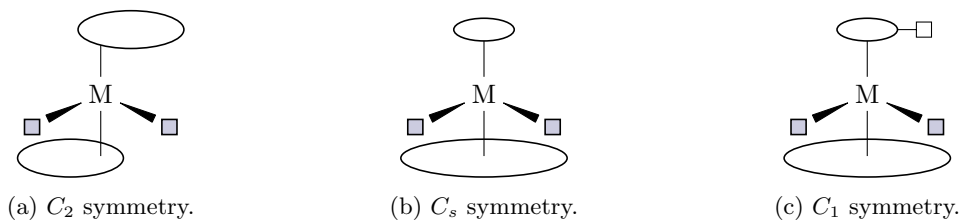(a) C_2 symmetry.   (b) C_s symmetry.   (c) C_1 symmetry.

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.
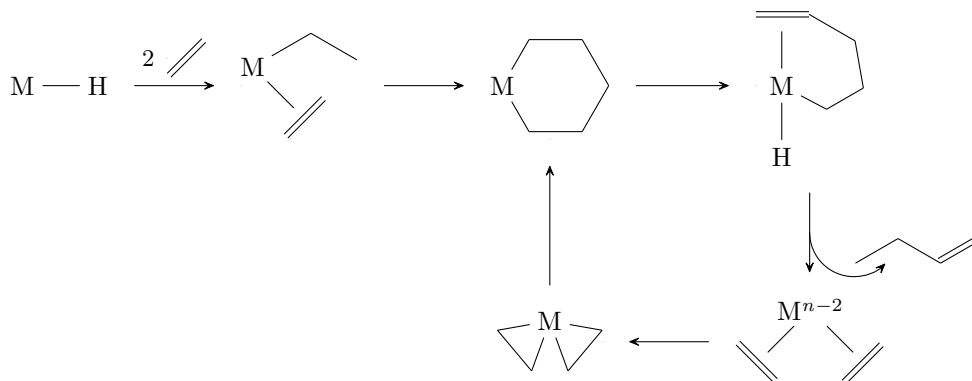
- Oligomerization mechanism:

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.

5.2 Office Hours (Anderson)

- Chain walking is when the metal bonds to a σ bond, moves to an adjacent carbon, moves to a double bond next, and on and on.

- The terminal olefins are sterically favored, even though the internal ones are typically thermodynamically favored.
- Early metals typically make linear polyolefins, while late metals prefer branched ones.

- What is the difference between a Chatt, distal, and alternating mechanism?

- Chatt and distal mechanisms are the same thing (known as Chatt due to Eurocentrism).

5.3 Discussion Section

5/11:
- HW5 is due 5/21/2021.

- Discussion recordings will be posted in the Panopto folder from now on, but there may be a delay.

- Point out dipole on CO in Homework 4.1a.

- Iron starts from Fe^I.

- Draws out and discusses the FeMoCO enzyme (which is actually an enzyme, not just iron, molybdenum, and a carbonyl ligand).
  - FeMoCO possibly binds to CO in bidentate fashion through two irons.
    - ■ This could support a Chatt mechanism since it would be easier to delocalize the higher oxidation state across two irons.
  - The iron in the center of FeMoCO that forms six partial bonds and doesn't really make any sense is sometimes called a **Texas iron**.

- Considers the 4-membered transition state and arrow-pushing for ROMP.

- It's good to know what the end groups are for the purposes of NMR.

- Goes over Figure 4.8 and Homework 4.4 in a bit more detail.

- Goes over Homework 3.