

# Unit 5

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## 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:

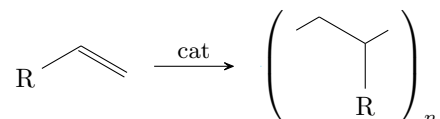
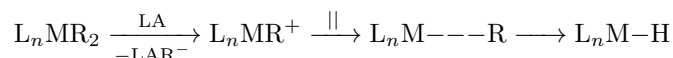


Figure 5.1: The general form of olefin polymerization.

- If  $\text{R} = \text{H}$ , we have polyethylene.
- If  $\text{R} = \text{Me}$ , we have polypropylene.
- This is a thermodynamically favorable, exothermic reaction since  $\pi$  bonds are weaker than  $\sigma$  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  $x$ . Also known as  $M_N$ .

- **Weight averaged molecular weight:** The quantity  $\frac{\sum N_x M_x^2}{\sum N_x M_x}$ . Also known as  $M_w$ .
- **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:**



- 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.
- $\beta$ -H elimination is the simplest way to terminate the chain, even though there are several possibilities.
- **Activation:**
  - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-AlR_4^-]{AlR_3/MAO} L_nMe^+$ .
  - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-MeBAr^F_4]{BAr^F_3} L_nMe^+$ .
  - $L_nMCl_2 \xrightarrow{AlR_3/MAO} L_nMMe_2 \xrightarrow[-CH_4]{HBAr^F_4} L_nMe^+$ .
  - 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:

- $\text{MR}(\text{||}) \longrightarrow \text{M}---\text{R} \xrightarrow{\text{||}} \text{M}(\text{||})(---\text{R}) \longrightarrow \text{M}---\text{R} \longrightarrow \longrightarrow \longrightarrow .$
- 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...
  - $\text{H}_2$ :  $\text{L}_n\text{M}-\text{pl} \xrightarrow{\text{H}_2} \text{L}_n\text{M}-\text{H} + \text{H}-\text{pl}$ , where pl is a polymer<sup>[1]</sup>.
  - $\beta$ -H elimination:  $\text{L}_n\text{M}---\text{pl} \longrightarrow \text{L}_n\text{M}(\text{H})(\text{||pl}) \longrightarrow \text{L}_n\text{M}-\text{H} + =-\text{pl}$ .
  - $\beta$ -H abstraction:  $\text{M}(\text{||})(---\text{pl}) \longrightarrow \text{M}(\text{Et})(\text{||pl}) \longrightarrow \text{MEt} + =-\text{pl}$ .

- The relative rates of growth vs. determination dictate the type of material we get.

- $K_p$  is the rate of growth/propagation;  $K_t$  is the rate of termination.
- $K_p$  vs.  $K_t$  dictates the product.
- $K_p \gg \gg K_t$  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**.
- $K_t \gg K_p$  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.

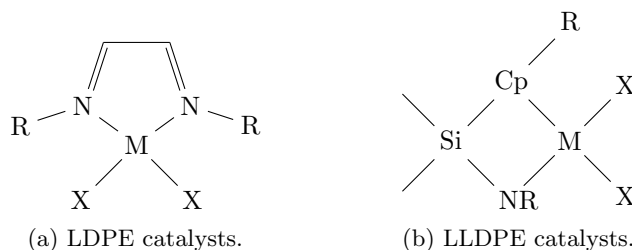


Figure 5.2: Polyethylene-type catalysts.

- 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:
  - $\text{TiCl}_x + \text{AlR}_x \longrightarrow$  a heterogeneous catalyst that's super active ( $> 10^9$  kg of polymer per gram of catalyst).
  - Note that  $x = 3$  or 4.
  - Alternate catalysts:  $\text{Cr}^{\text{III}} + \text{silica} \xrightarrow{\text{O}_2, \Delta} \text{CrO}_4 \xrightarrow{\text{||}} \text{reduced Cr center (the active catalyst)}.$

<sup>1</sup>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  $\beta$ -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 crystalline, highest melting point material.
- **Atactic** (polypropylene): Every methyl group is random.
  - The least crystalline, 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:

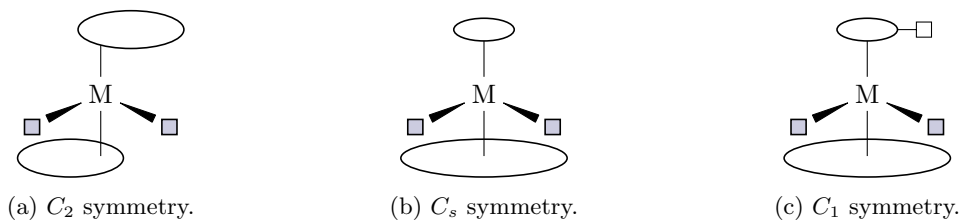


Figure 5.3: Polypropylene-type catalysts.

- 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  $\beta$ -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.

