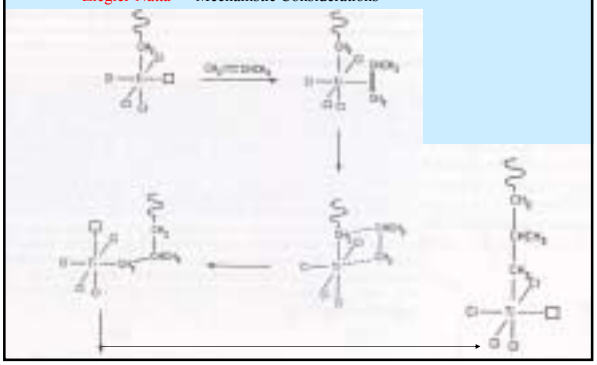
Stereochemistry

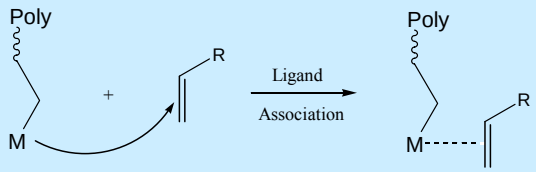
Ziegler-Natta Mechanistic Considerations



Coordination Polymerization

Ziegler-Natta

Propagation

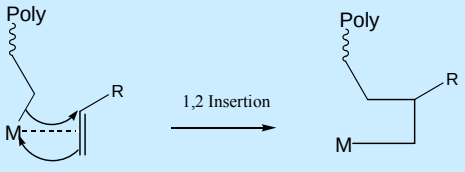


M = Ti, V with Al-MAO cocat

Coordination Polymerization

Ziegler-Natta

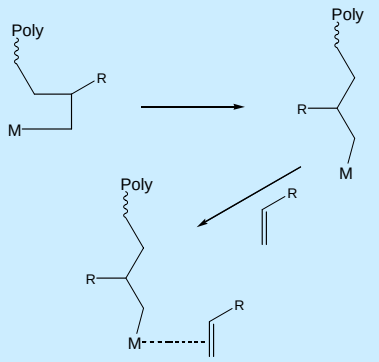
Propagation



Coordination Polymerization

Ziegler-Natta

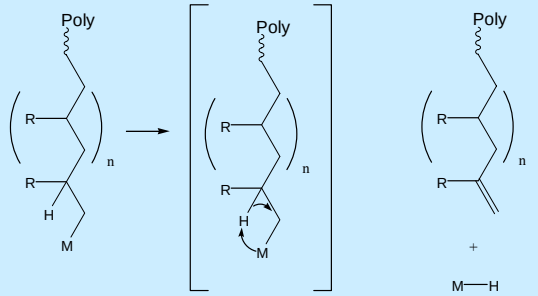
Propagation



Coordination Polymerization

Ziegler-Natta

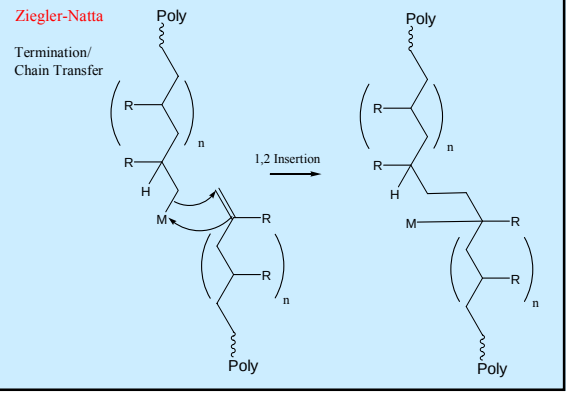
Termination/
Chain Transfer



Coordination Polymerization

Ziegler-Natta

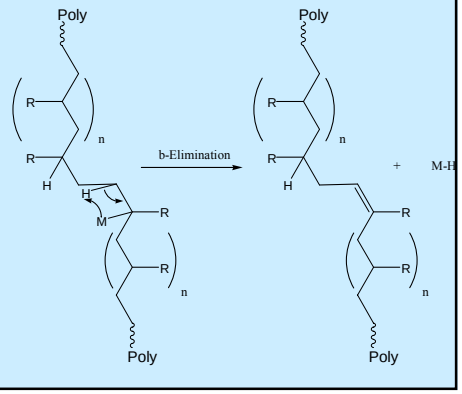
Termination/
Chain Transfer



Coordination Polymerization

Ziegler-Natta

Termination/
Chain Transfer



Coordination Polymerization

"Single-Site" Catalyst Revolution

Problem with Ziegler-Natta (Heterogeneous Catalysts)

Different types of active sites, each has its own kinetics

a. Different polymer rates
b. Different polymer structural outcomes
c. Different Chain Transfer
d. Different tolerances for comonomer incorporation

↓

Control of these factors empirical → large body of empirical research

Coordination Polymerization

"Single-Site" Catalyst Revolution

Definition of Single-Site Catalyst: Single Molecular Entity of Structure:

L_nMR

L_n = organic ligands: modify the activity of the metal
M = metal center, active catalyst
R = the polymer or initiating group

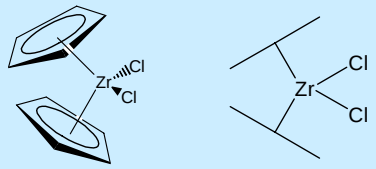
Advantages of Single Site Catalysts:

1. Characterizable Catalyst: not an unknown mixture,
   use typical synthetic analyses NMR, IR, MS
2. Control of Catalytic Reactivity: Living polymerization, low PDI
3. Design and Control of Stereochemistry (Tacticity)
4. Design and Control of Comonomer Incorporation
5. Can relate properties of polymerization to the catalyst structure

Coordination Polymerization

Metallocenes: Started "Single-Site" Catalyst Revolution

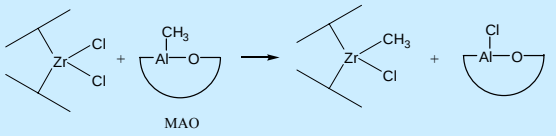
Big Example: Zirconocene

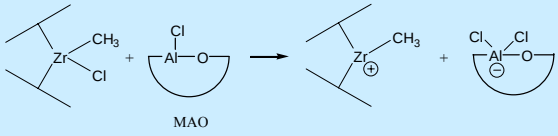


Coordination Polymerization

Zirconocene Polymerization

Initiation

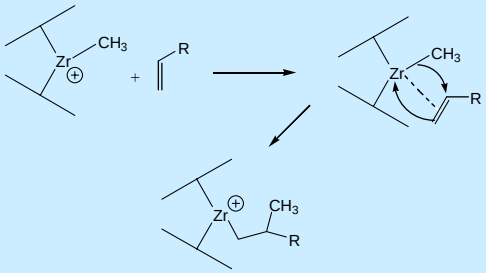




Coordination Polymerization

Zirconocene Polymerization

Propagation



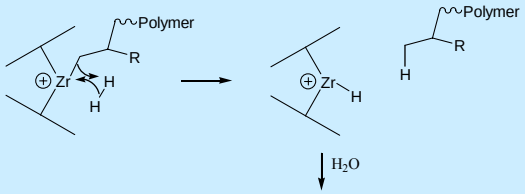
Coordination Polymerization

Zirconocene Polymerization

Termination: Polymerization is essentially living:

Bulky ligands on catalyst prevent chain transfer

Quench with hydrogen, water

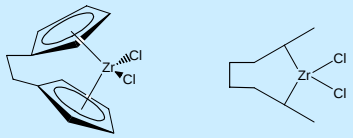


Coordination Polymerization

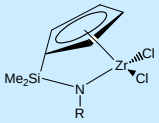
Zirconocene Polymerization

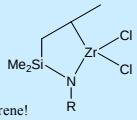
Activity/Rate Control: *ansa* catalysts

Waymouth, R.M., McKnight, A.L.; *Chem. Rev.* **1998**, *98*, 2587-2598



Comonomer Incorporation: *ansa*-monocyclopentadienyl-amido (CpA) catalysts



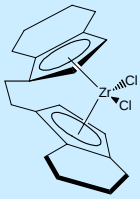


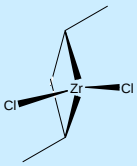
can even accept styrene!

Coordination Polymerization

Zirconocene Polymerization

Chiral Catalysts



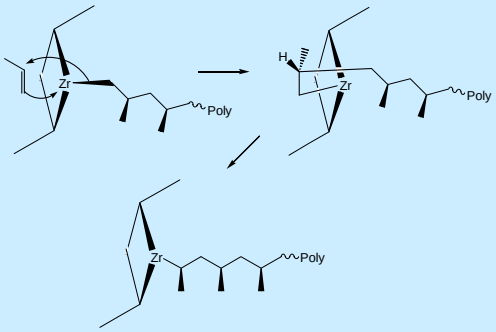


Coates, G.; *Chem. Rev.* **2000**, *100*, 1223-1252

Coordination Polymerization

Zirconocene Polymerization

Chiral Catalysts

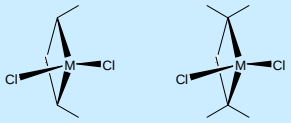


Coordination Polymerization

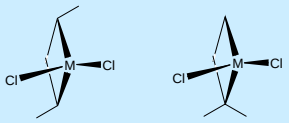
Zirconocene Polymerization

Chiral Catalysts

Polymer Chain End Control:



Enantiomorphic Control:

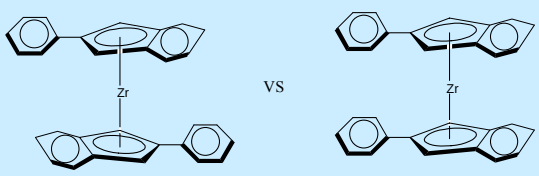


isospecific syndiospecific

Coordination Polymerization

Zirconocene Polymerization

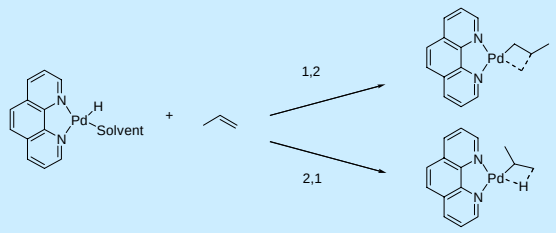
Cool Chiral Catalysts



Isotactic block Atactic block

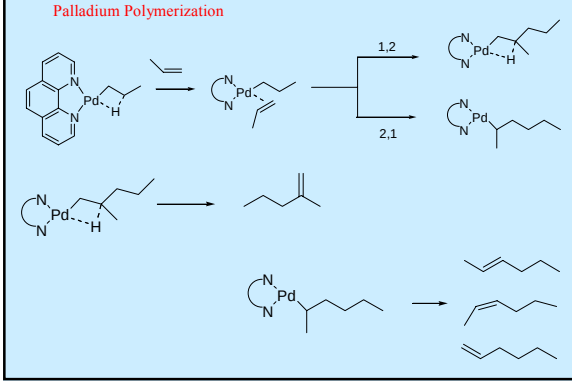
Coordination Polymerization

Palladium Polymerization



Coordination Polymerization

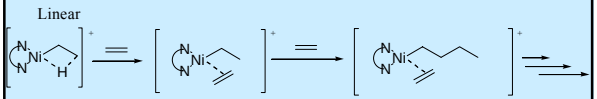
Palladium Polymerization



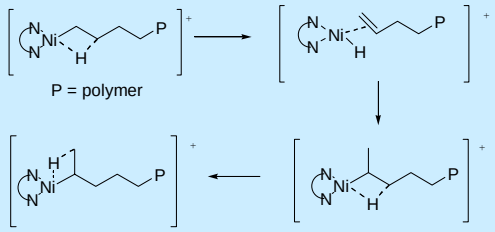
Coordination Polymerization

Palladium Polymerization

Linear

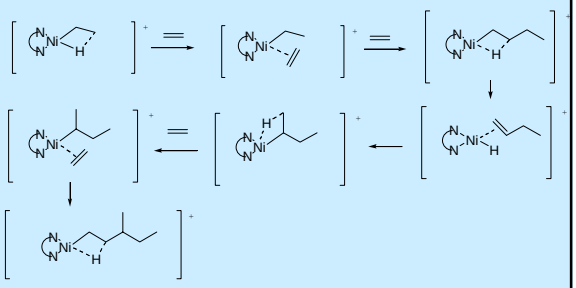


Branching



Coordination Polymerization

Palladium Polymerization



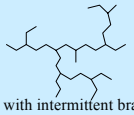
Coordination Polymerization

Polyethylene

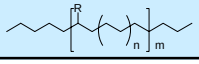
3 Major Classes:

1. HDPE: linear, semi-crystalline, T_m = 135°C, usually made with Ziegler-Natta catalysts, higher strength, low processability

2. LDPE: branched homopolymer, usually high temp, high pressure radical, low strength, high processability

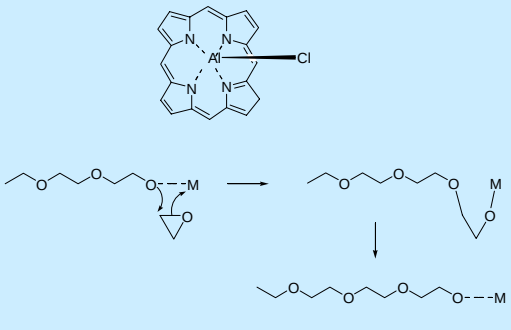


3. LLDPE: linear with intermittent branching, get higher strength properties with better processability



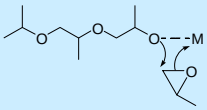
Coordination Polymerization

Porphoryn Polymerization

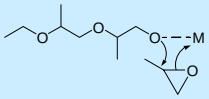


Coordination Polymerization

Porphoryn Polymerization



Favored by anionic



Favored by cationic, depending how big substituent is. Also favored for Porphoryn catalysts

So, although coordination polymerization Is usually attributed to being anionic in Character, that is not always true