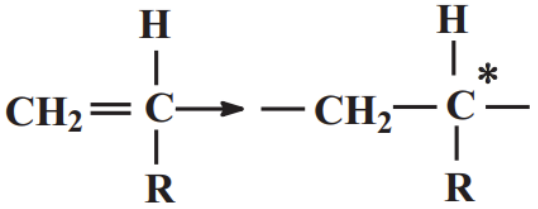
Stereochemistry of Polymerization

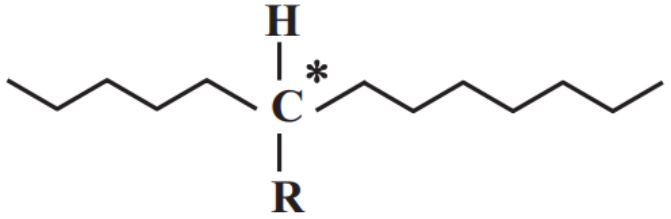
16:160:509 – Polymer Chemistry

Lecture 15 to 16

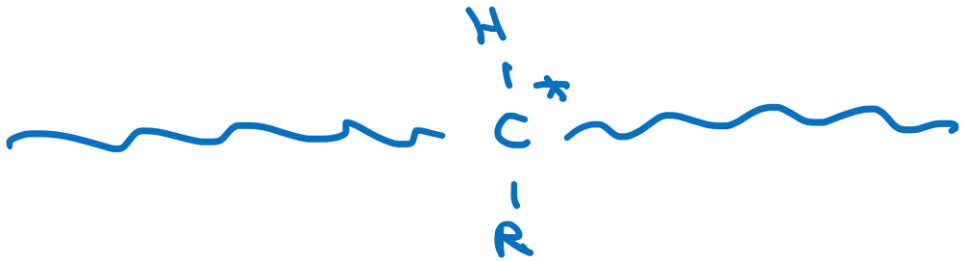
RUTGERS
School of Arts and Sciences
DEPARTMENT OF CHEMISTRY
AND CHEMICAL BIOLOGY

Polymers May Have Stereogenic Centers That Are Pseudochiral

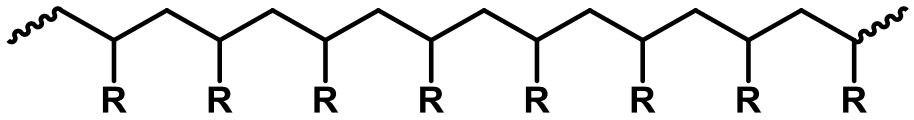


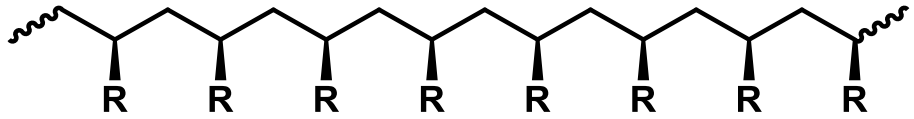


Strictly speaking, this stereogenic center is chiral, with four distinctly different substituents bonded to it. However, two of these substituents are the long arms of the polymer chain, each often consisting of hundreds or thousands of atoms, making the chain molecule and its mirror image "almost" superposable. Therefore, this stereogenic center does not cause a detectable rotation of plane-polarized light, and the polymer does not exhibit optical activity. We thus refer to such a stereogenic center as a "**pseudochiral**" center.

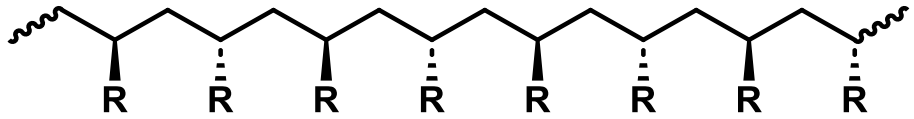


Tacticity Is a More Important Stereochemical Parameter for Polymers

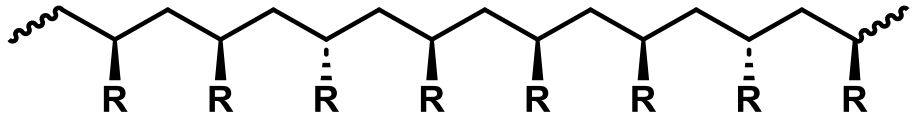




Isotactic

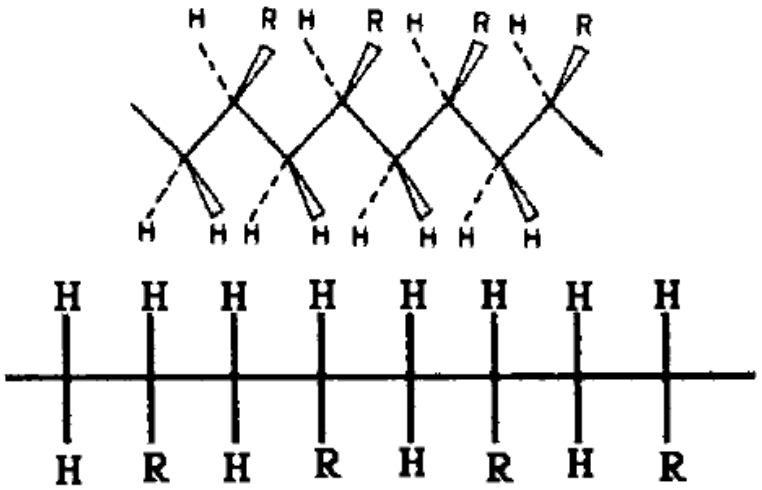


Syndiotactic

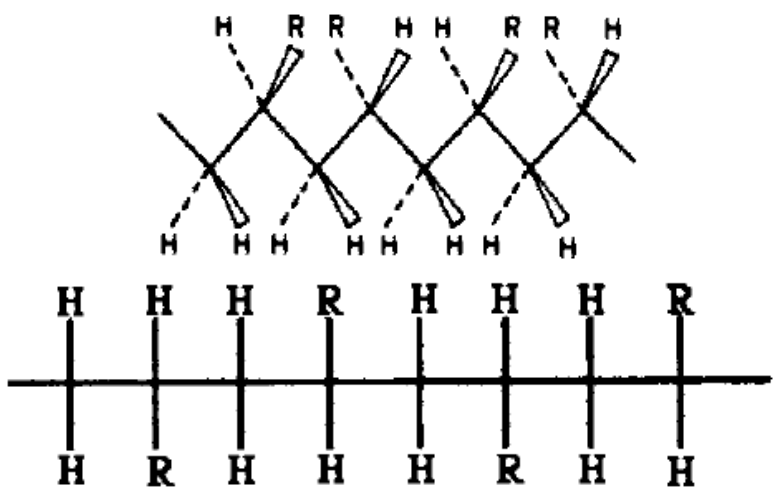


Atactic

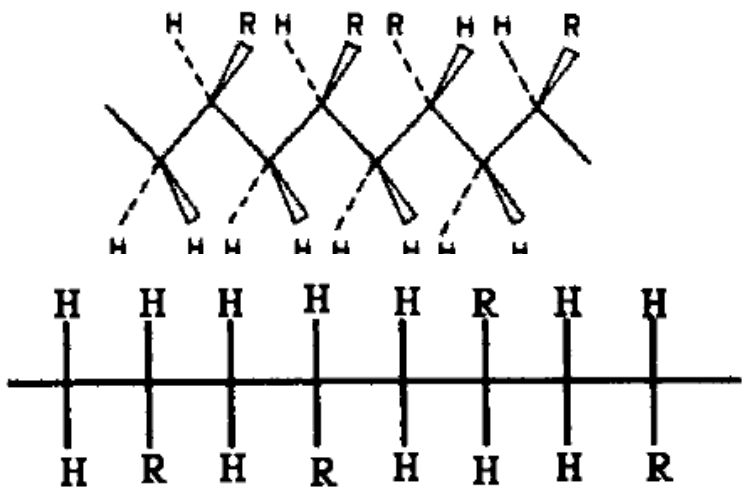
Isotactic



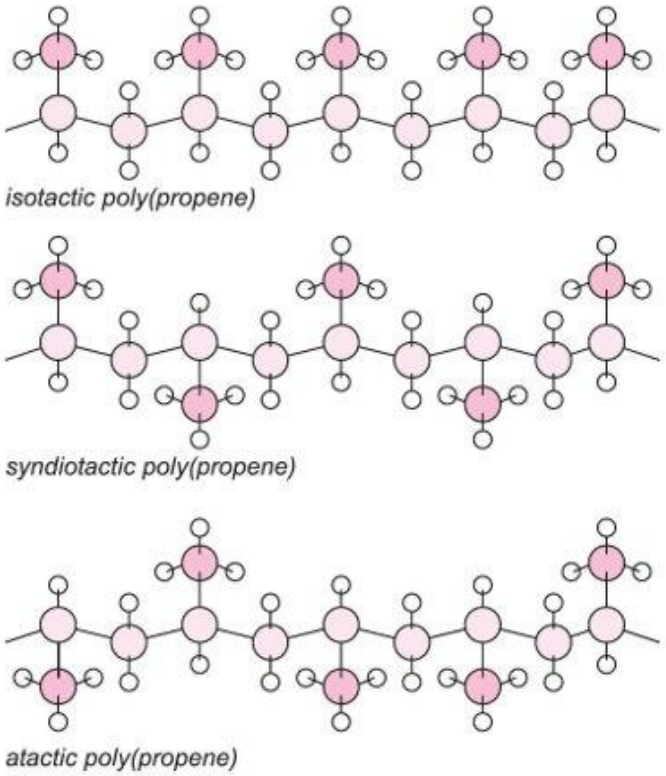
Syndiotactic

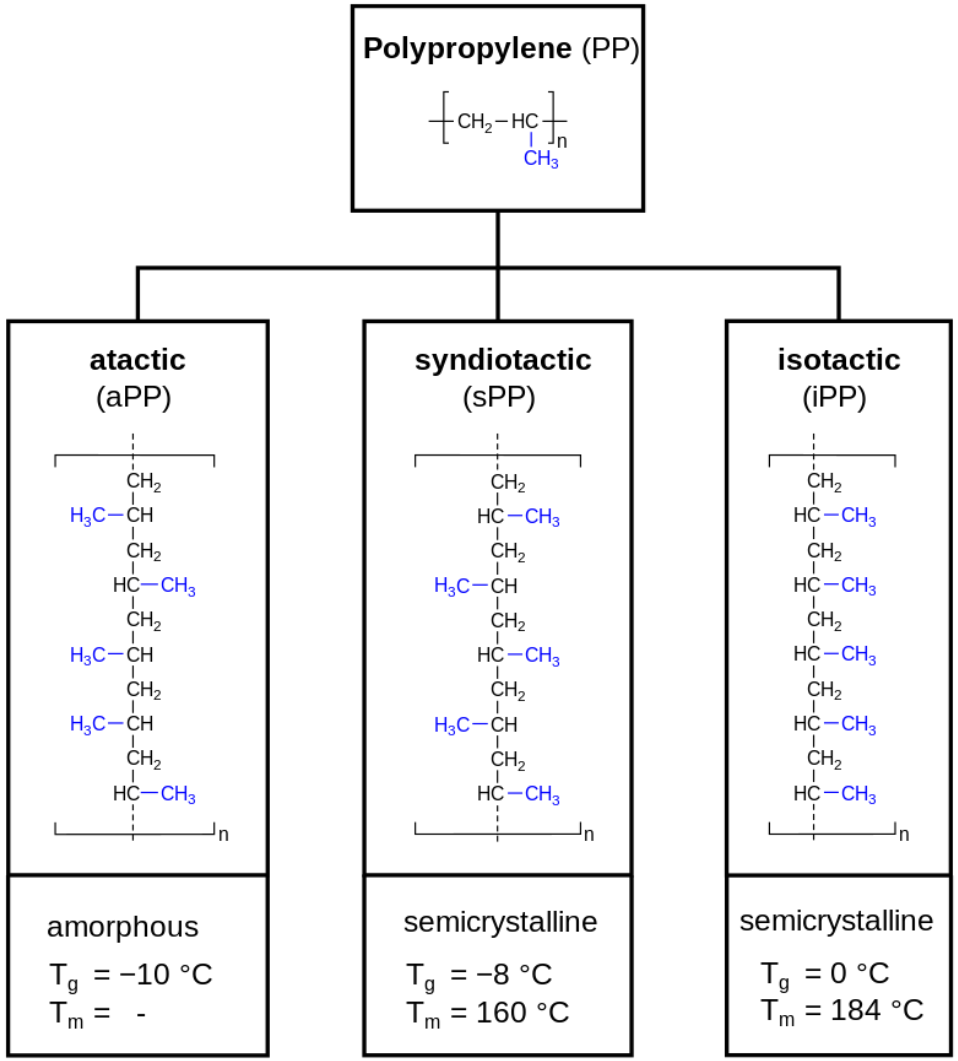


Atactic



The Macroscopic Properties of Polymers Are Dictated by Tacticity



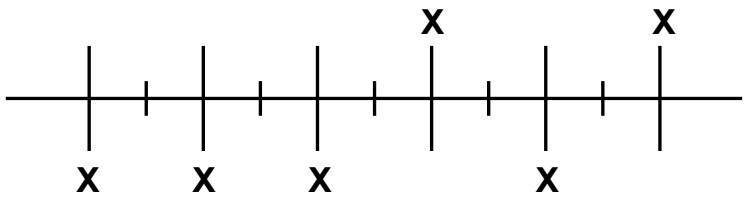


This one is used in everyday products

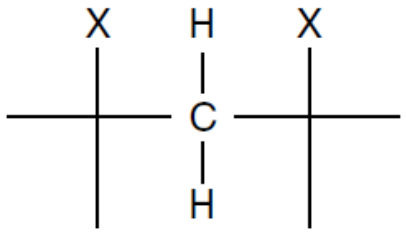
Atactic polypropylene
- Amorphous (cannot crystallize)
- Very gooey and waxy
- No commercial application

Isotactic polypropylene
- Semi-crystalline
- Superior properties
- 74 million tonnes annually

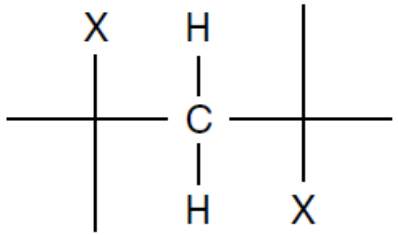
What Parameters Do We Use to Characterize the Stereoregularity of a Given Polymer?



Dyads



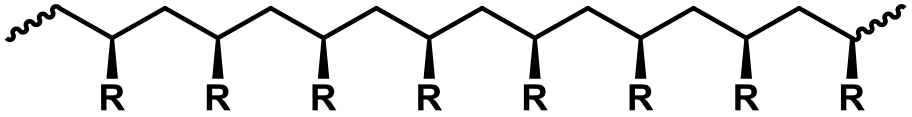
meso (*m*) dyad



racemic (*r*) dyad

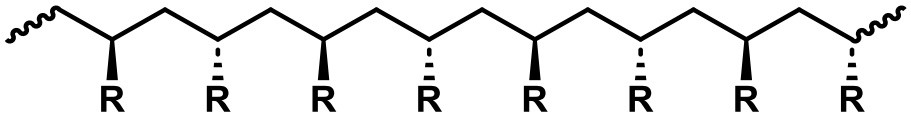
Define p_m and p_r as the probability of addition occurring in the *meso* and *racemic* modes, respectively.

$$p_m + p_r = 1$$



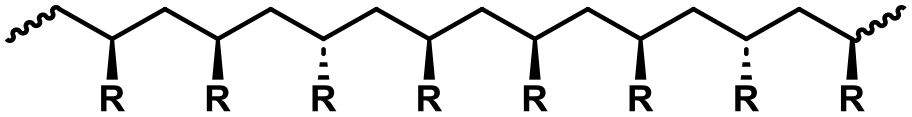
Isotactic

$p_m = 1, \quad p_r = 0$



Syndiotactic

$p_m = 0, \quad p_r = 1$

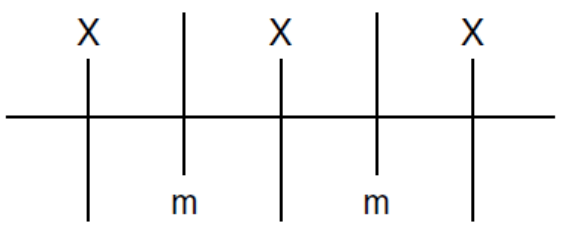


Atactic

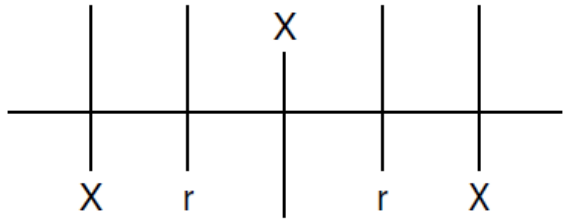
$0 < p_m < 1, \quad 0 < p_r < 1, \quad p_m + p_r = 1$

What Parameters Do We Use to Characterize the Stereoregularity of a Given Polymer?

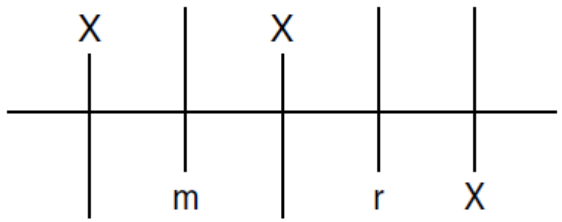
Triads



Isotactic triad (*mm*)

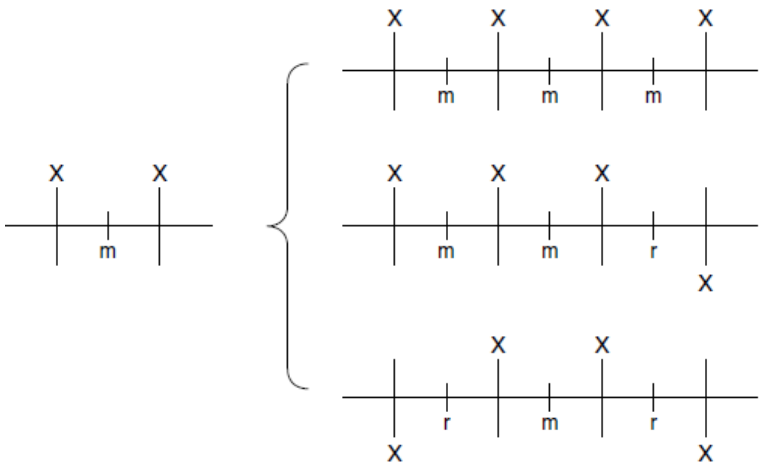


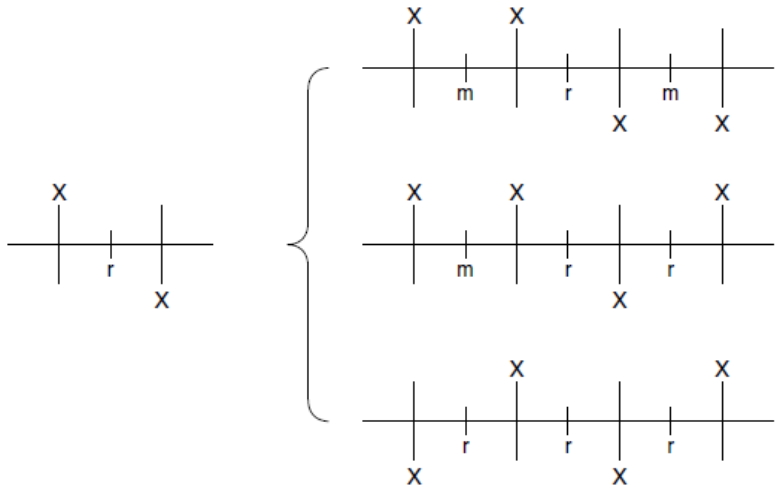
Syndiotactic triad (*rr*)



Heterotactic triad (*mr*)

We can even go further for tetrads, pentads, hexads, etc.

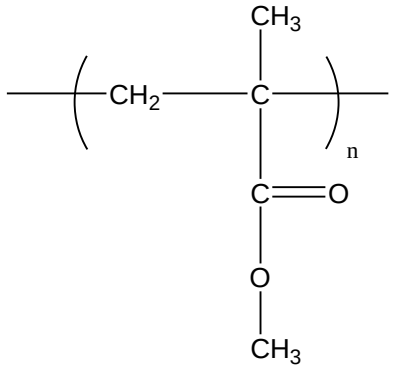


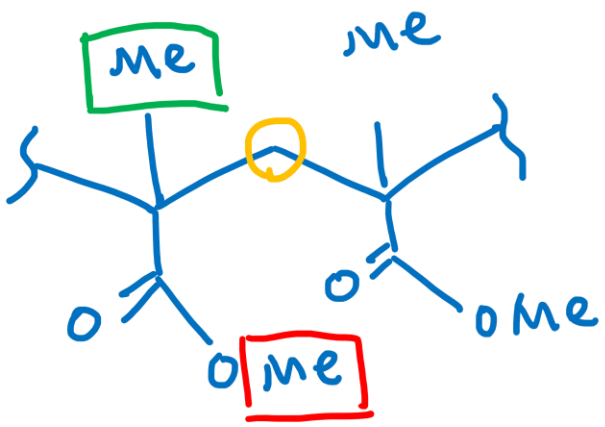


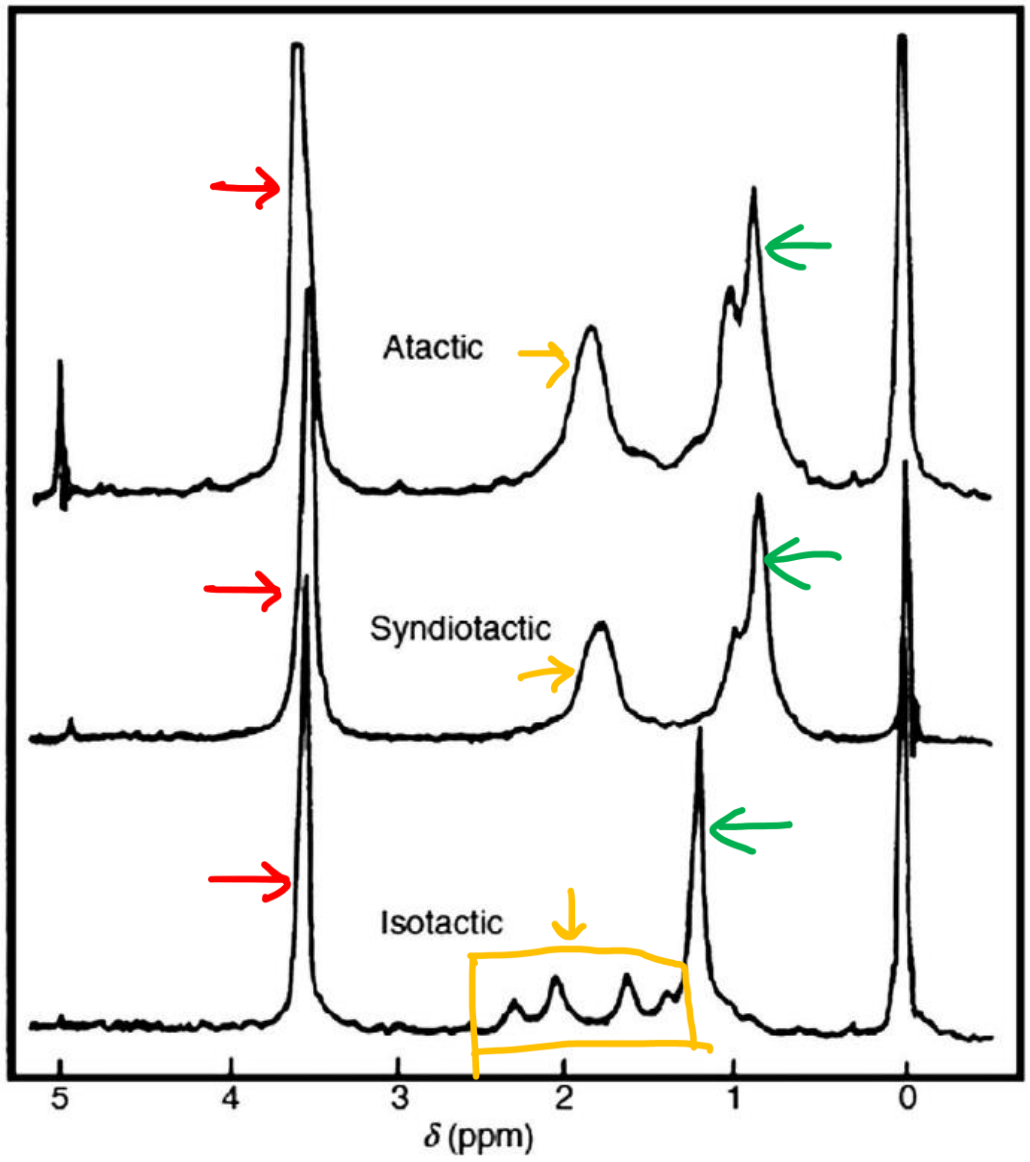
The higher the order, the more complete stereo information you will obtain about the polymers, but the measurements will become progressively more challenging. We will limit our discussion to dyads and triads.

Measurement of Stereoregularity Using NMR

Let's take poly(methyl methacrylate) (PMMA) as an example



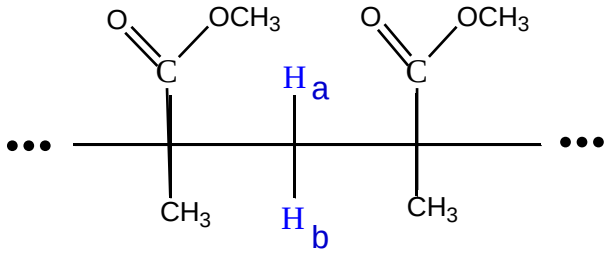




Measurement of Dyads Using NMR

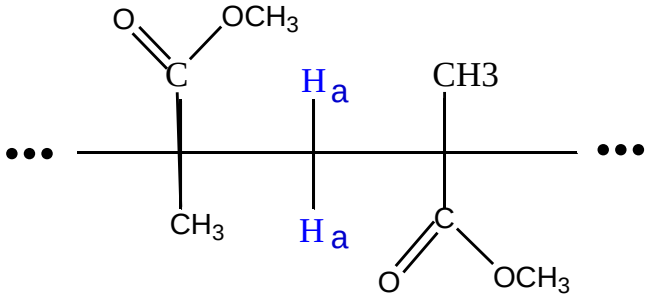
Methylene Perspective

***meso* (*m*) dyad**



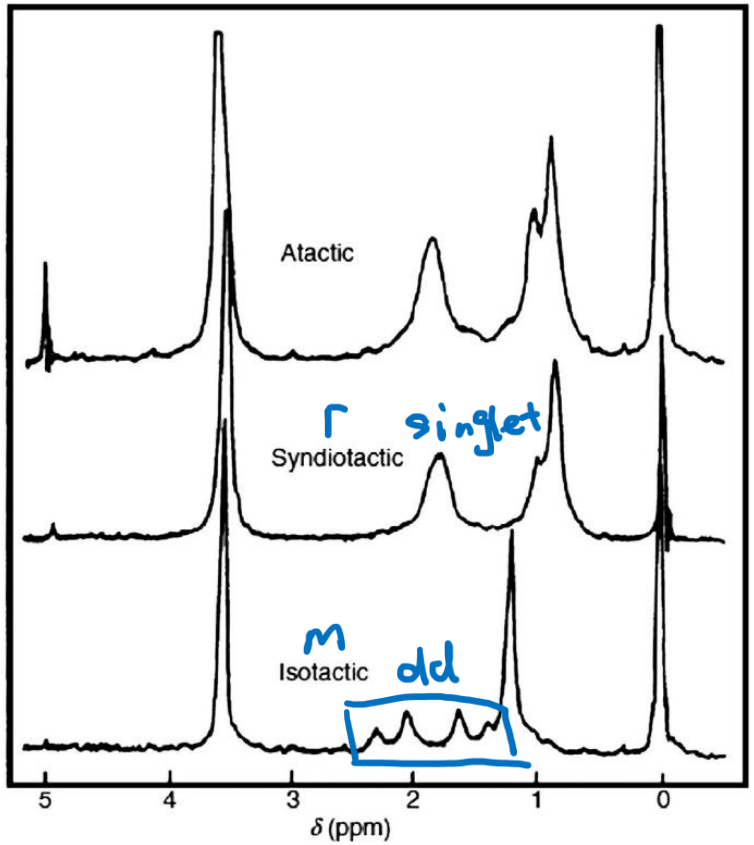
Diastereotopic protons
(NMR distinguishable – AB quartet)

***racemic* (*r*) dyad**

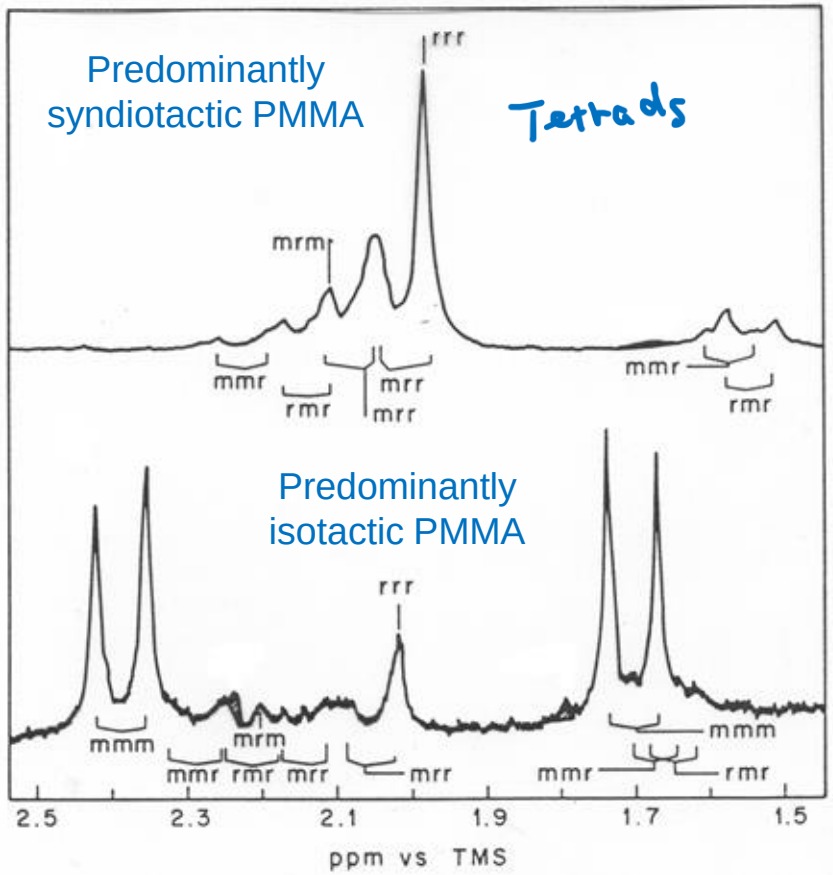


Homotopic protons
(NMR indistinguishable – singlet)

60 MHz NMR



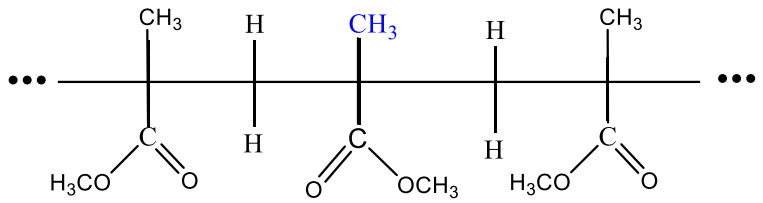
220 MHz NMR



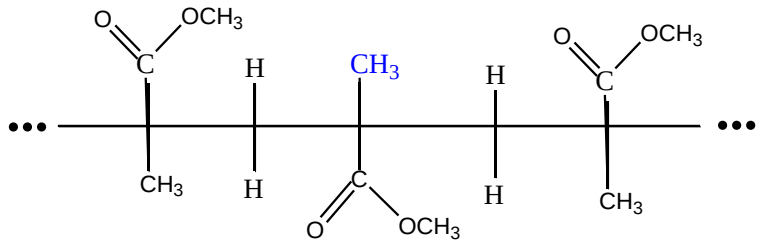
Two (or more precisely, an even number of) monomer units are required to utilize the methylene protons for characterizing stereochemistry. The chemical environment of the methylene protons is defined by dyads (or tetrads, hexads, etc.).

Measurement of Triads Using NMR

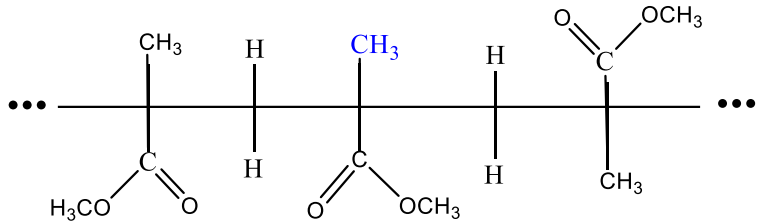
Methyl Perspective



Isotactic triad (*mm*)

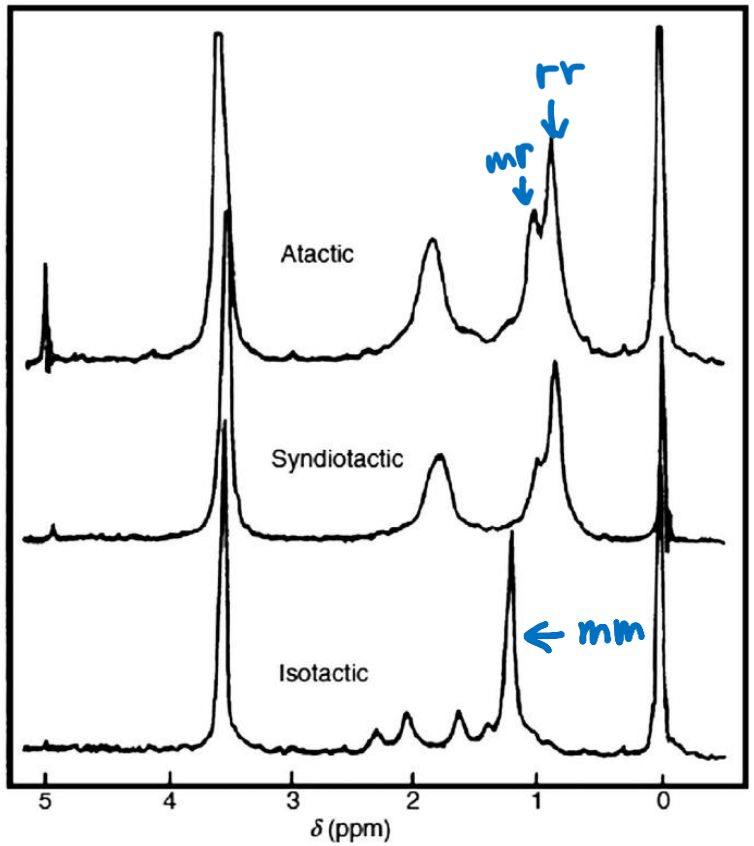


Syndiotactic triad (*rr*)

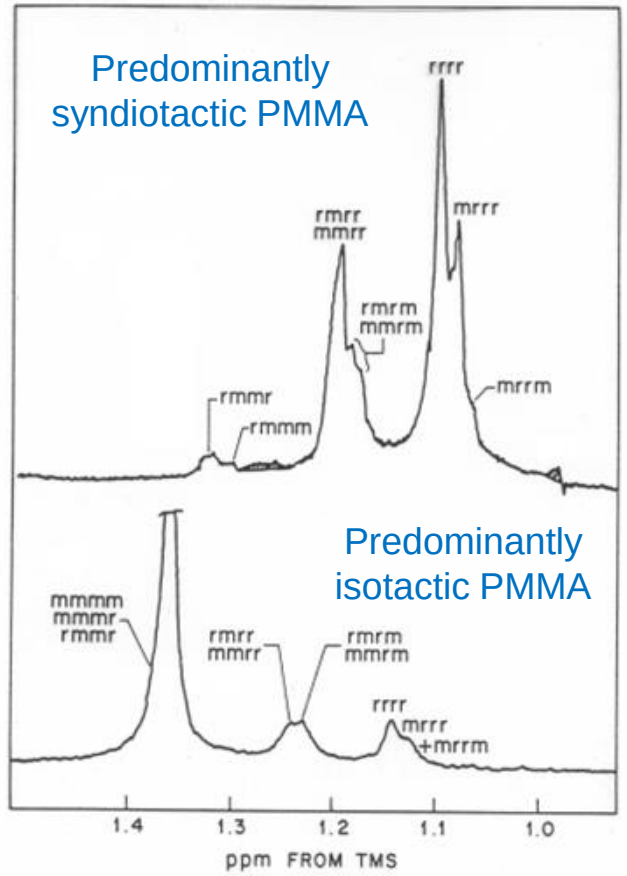


Heterotactic triad (*mr*)

60 MHz NMR



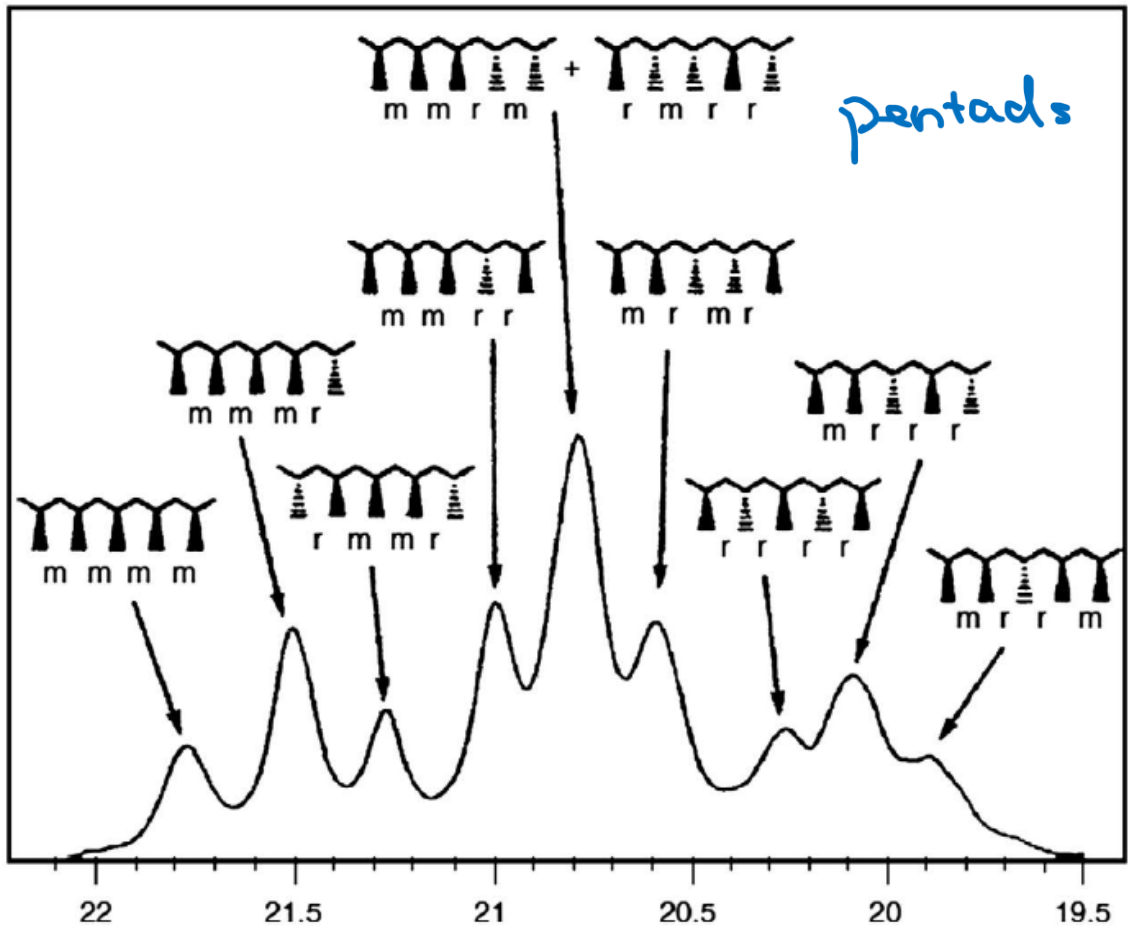
220 MHz NMR



Three (or more precisely, an odd number of) monomer units are required to utilize the methyl protons for characterizing stereochemistry. The chemical environment of the methylene protons is defined by triads (or pentads, heptad, etc.).

Measurement of Stereoregularity Using ^{13}C NMR

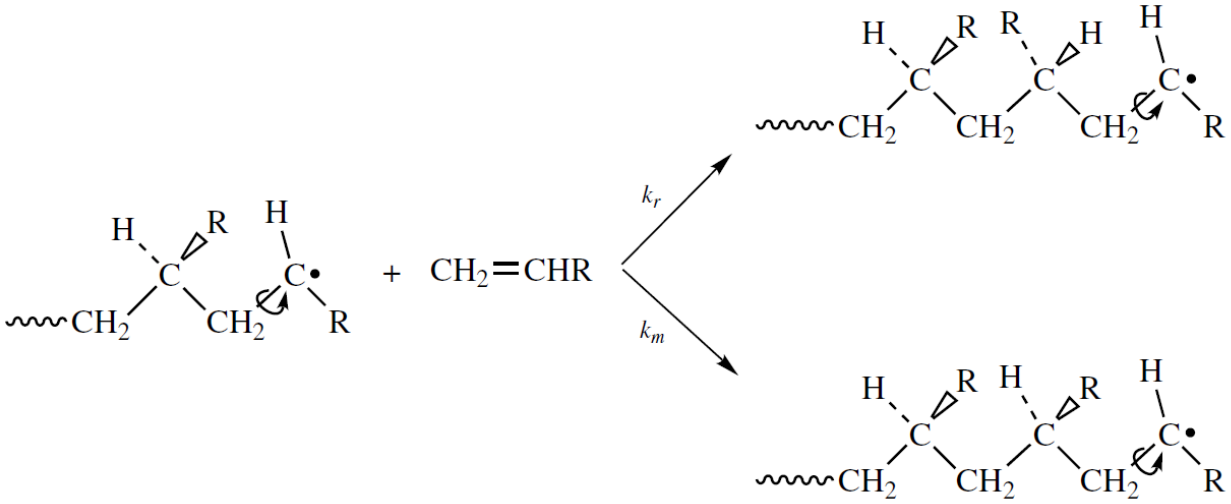
100 MHz NMR



Pretty much an atactic PP

^{13}C NMR assignments for polypropylene

Stereoselectivity in Free-Radical Polymerization



- **A slight preference for syndiotactic placement over isotactic placement** due to steric and/or electrostatic repulsions between substituents in the polymer chain.
- This mechanism for syndioselective polymerization is referred to as ***polymer chain end control***—the addition of a monomer is influenced mostly by the configuration of the previous repeat unit.
- Since radical polymerizations are generally carried out at moderately high temperatures, which eliminate the slight preference for syndiotactic over isotactic placement, most of the resulting polymers are highly atactic. However, the exact extent highly depends on the substituents:

Poly(vinyl chloride) synthesized at 60°C is atactic: $p_r \approx p_m \approx 0.5$

Poly(methyl methacrylate) synthesized at 100°C is predominantly syndiotactic: $p_r \approx 0.73$

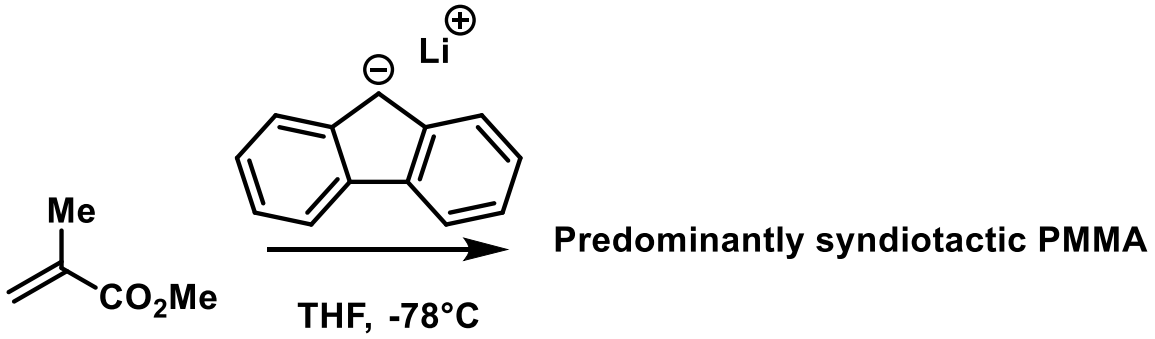
How to rationalize this?

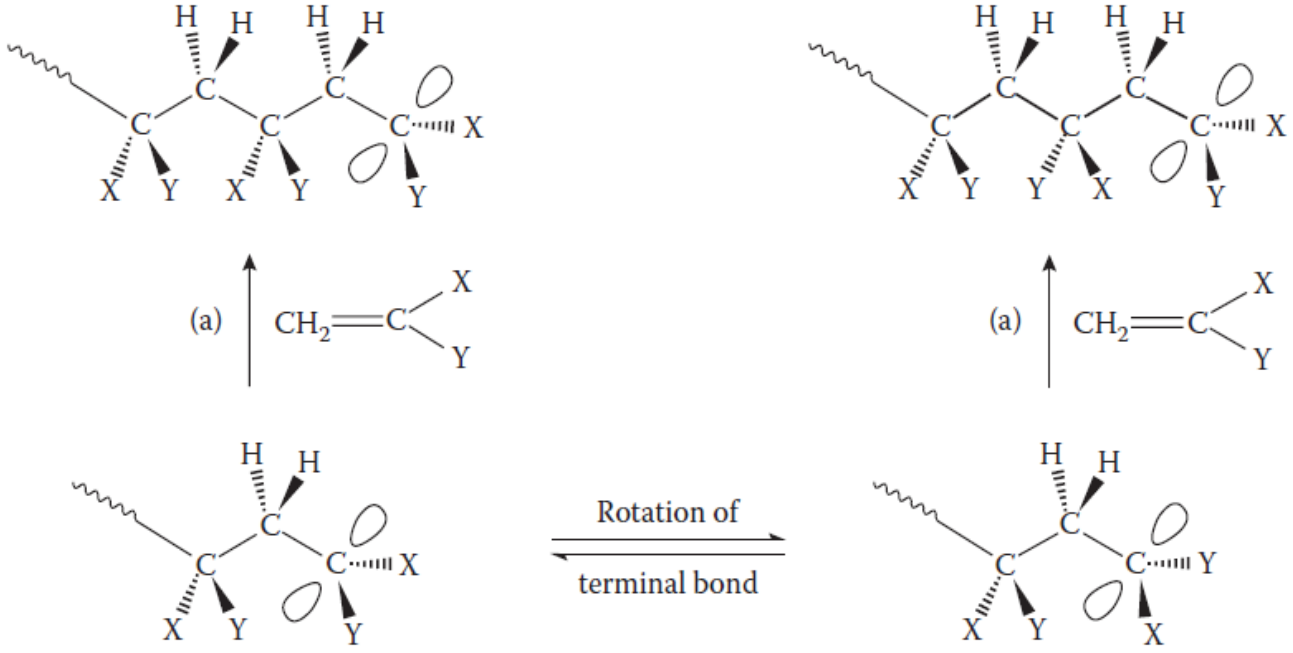
Stereoselectivity in Ionic Polymerization

Cationic or anionic polymerization exhibits stereoselectivity in the following two scenarios:

Scenario 1: *Polar solvents and low temperature*

In polar solvents, the polymerization involves solvent-separated ion-pairs or free-ion-propagating species, where the stereochemistry is influenced by factors similar to those in radical polymerization. Consequently, highly syndiotactic polymers can be formed due to analogous steric and electrostatic effects.





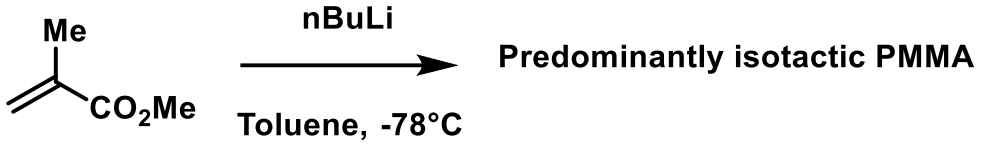
Syndiotactic placement reduces the steric and/or electrostatic repulsion between substituents.

Polymer chain end control

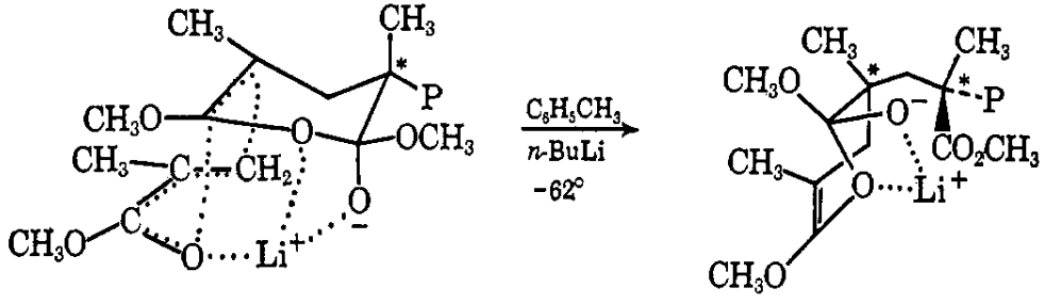
Stereoselectivity in Ionic Polymerization

Scenario 2: *Non-polar solvents, low temperatures, small counter-ions with strong coordinating power, and monomers containing polar substituent groups that serve as coordination sites.*

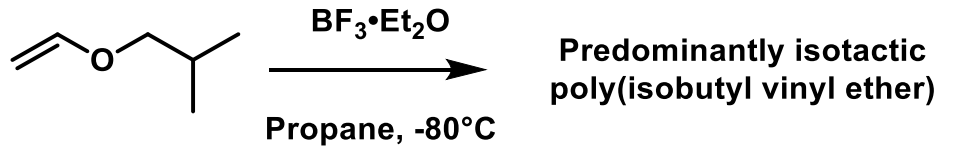
All these conditions are to promote ion-pair association, where strong coordination occurs between the counter-ion, the terminal units in the polymer chain, and the incoming monomer molecule. This may lead to highly isotactic polymers.



Anionic coordination mechanism (Li > Na >> K, Cs)



(Proposed by Cram in 1968)



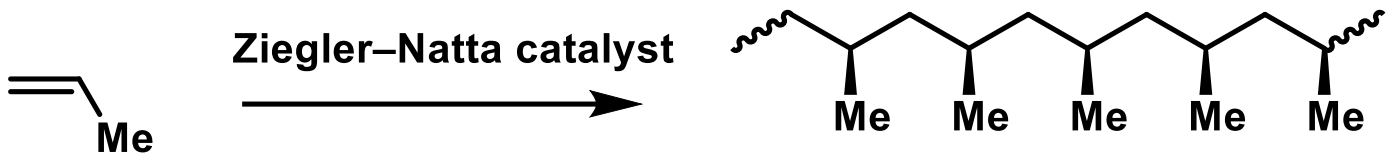
Cationic coordination mechanism

The first reported stereoselective polymerization (1947), where a semicrystalline polymer was obtained. Initially, the crystallinity was attributed to a syndiotactic structure. However, in 1956, Natta used X-ray diffraction to reveal that the polymer was, in fact, isotactic.

Polymer chain end control

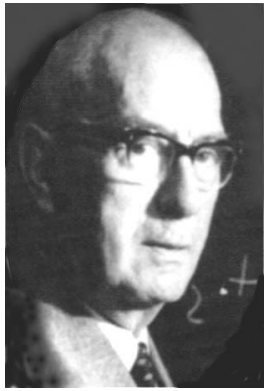
Ziegler–Natta Catalyst

- The use of ionic coordination polymerization for the preparation of highly stereoregular polymers faces several limitations, the most obvious being the need for polar functional groups to coordinate with counter-ions.
- The use of transition metals is a great approach to achieve stereoselective polymerization of non-polar monomers.

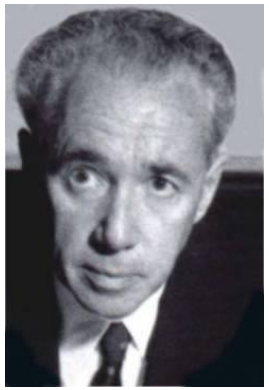


Isotactic polypropylene

Ziegler–Natta catalyst: $TiCl_4$ + $Al(C_2H_5)_3$



Karl Ziegler



Giulio Natta

- First discovered by Karl Ziegler (in the form of $TiCl_4$ + $Al(C_2H_5)_2Cl$) in 1953 for preparation of linear polyethylene (HDPE).
- Ziegler then disclosed his catalyst to the Montecatini Company in Italy, for which Giulio Natta was acting as a consultant. Natta became interested in the catalyst and discovered its use (in the form of $TiCl_3$ + $Al(C_2H_5)_3$)in synthesis of isotactic polypropylene in 1954.
- In the current form used by industry, $MgCl_2$ is often added to enhance the activity of the titanium-based catalysts.

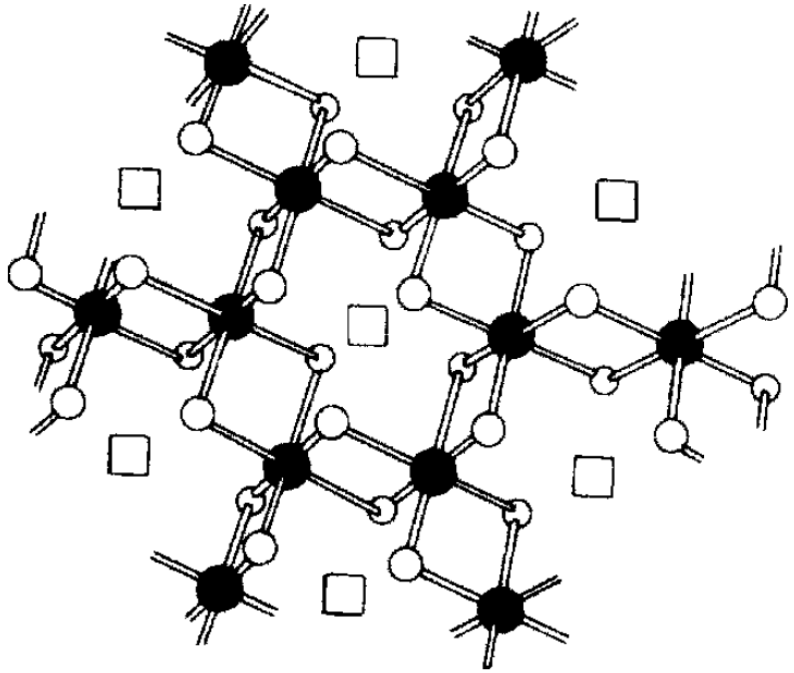
Mechanism of Ziegler–Natta Catalyst

The actual form of the catalyst is $TiCl_3$

$$TiCl_4 + AlR_3 \longrightarrow TiCl_3R + AlR_2Cl$$

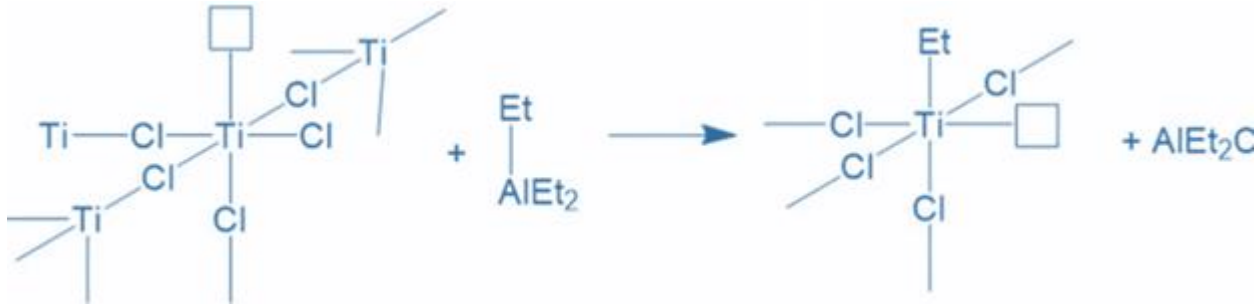
$$TiCl_3R \longrightarrow TiCl_3 + R\bullet$$

$$R\bullet \longrightarrow \text{combination} + \text{disproportionation}$$



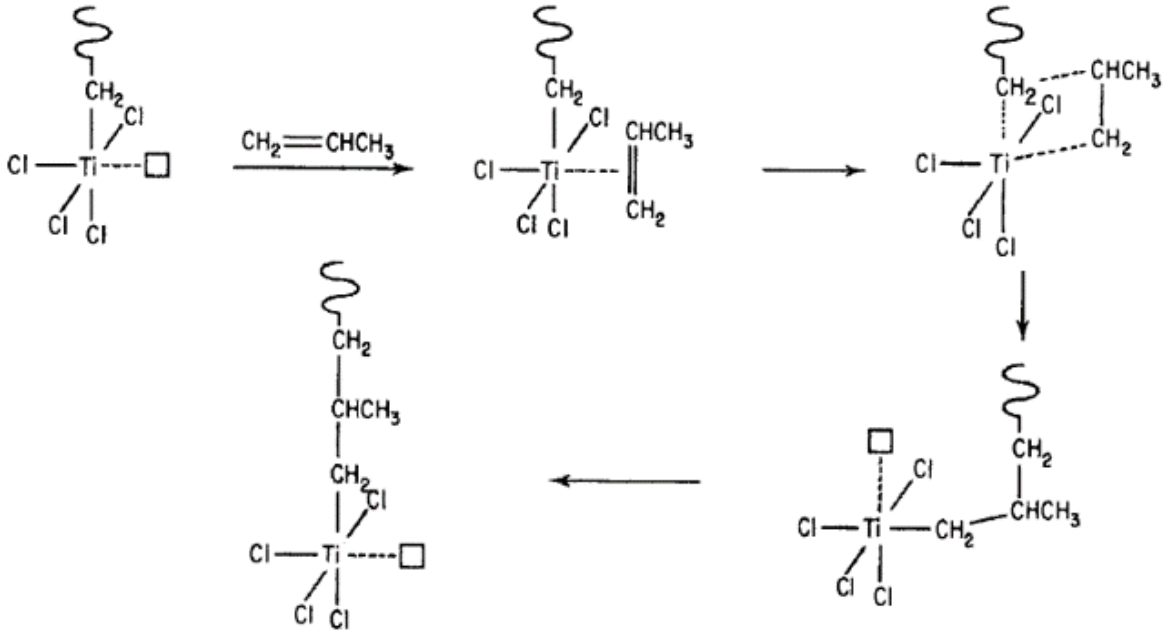
Crystal structure of α-$TiCl_3$

Polymerization occurs at active sites found on the edges (surfaces) of the $TiCl_3$ crystal, where a titanium atom at the surface is bonded to only five chlorines instead of six.

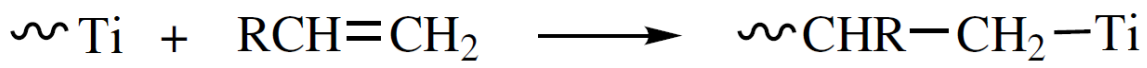


Mechanism of Ziegler–Natta Catalyst

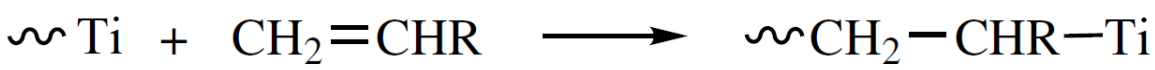
Propagation (*Cossee-Arlman mechanism*):



- *Primary insertion*



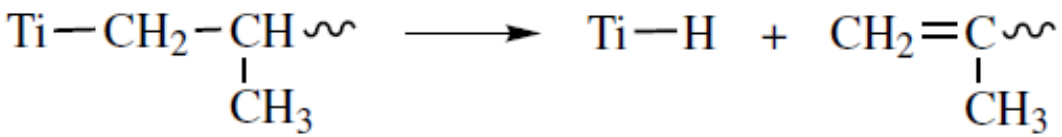
Primary insertion



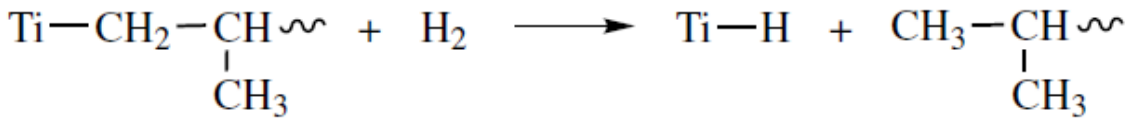
Second insertion

- *The chain must migrate to the original site to ensure the formation of an isotactic structure.*

Termination:

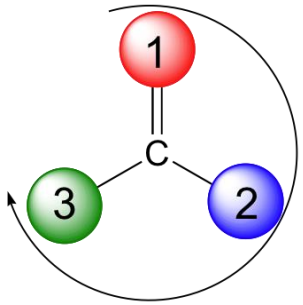


β-Hydride transfer (built-in mechanism)

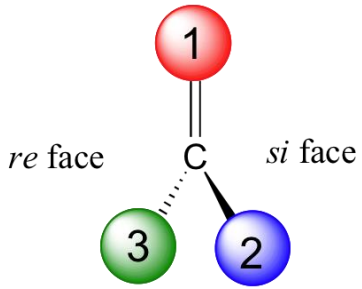


Chain transfer to hydrogen
(a good way to control molecular weight)

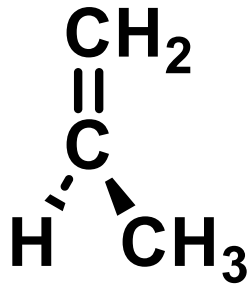
Origin of Stereoselectivity

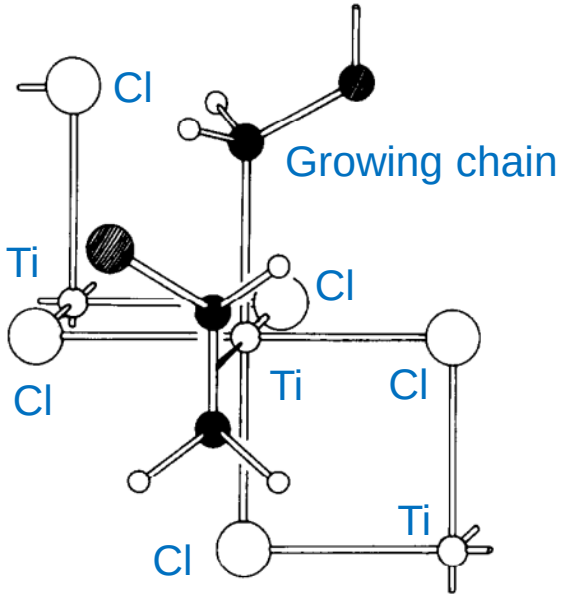


looking down on *re* face

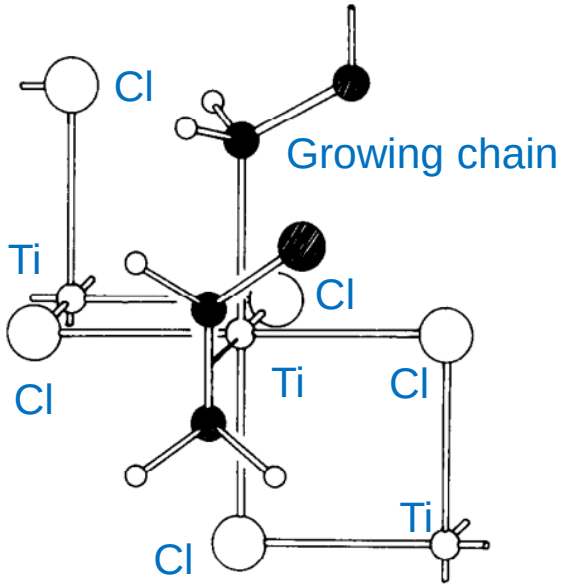


Propene is prochiral

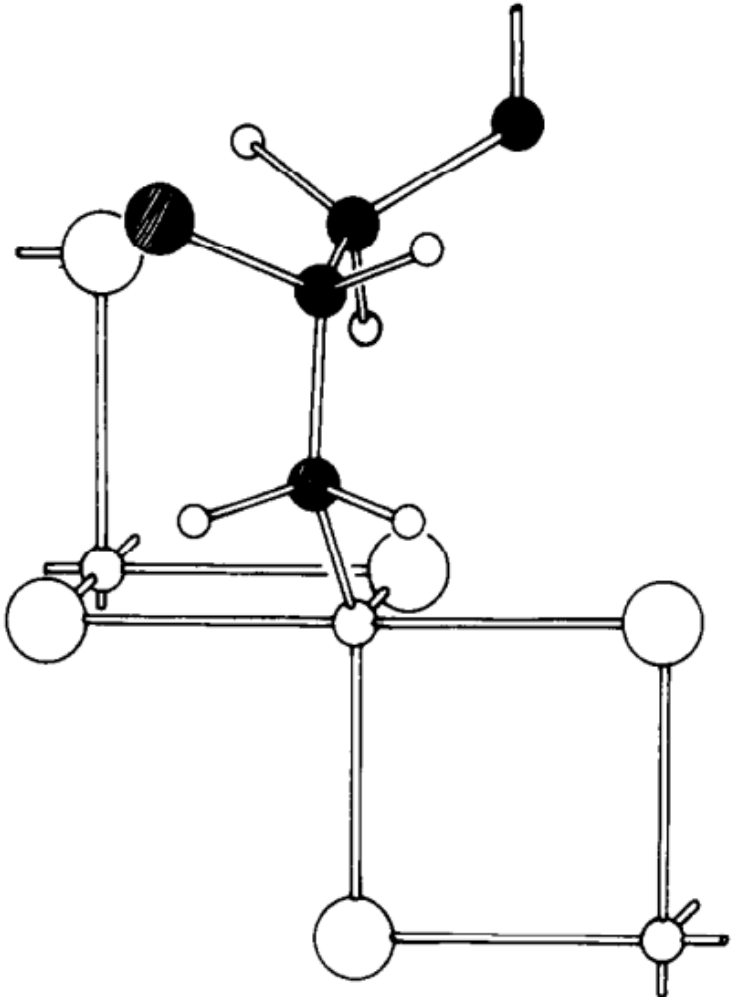




Ti coordinates with the *si* face of propene **(favored)**



Ti coordinates with the *re* face of propene **(less favored)**



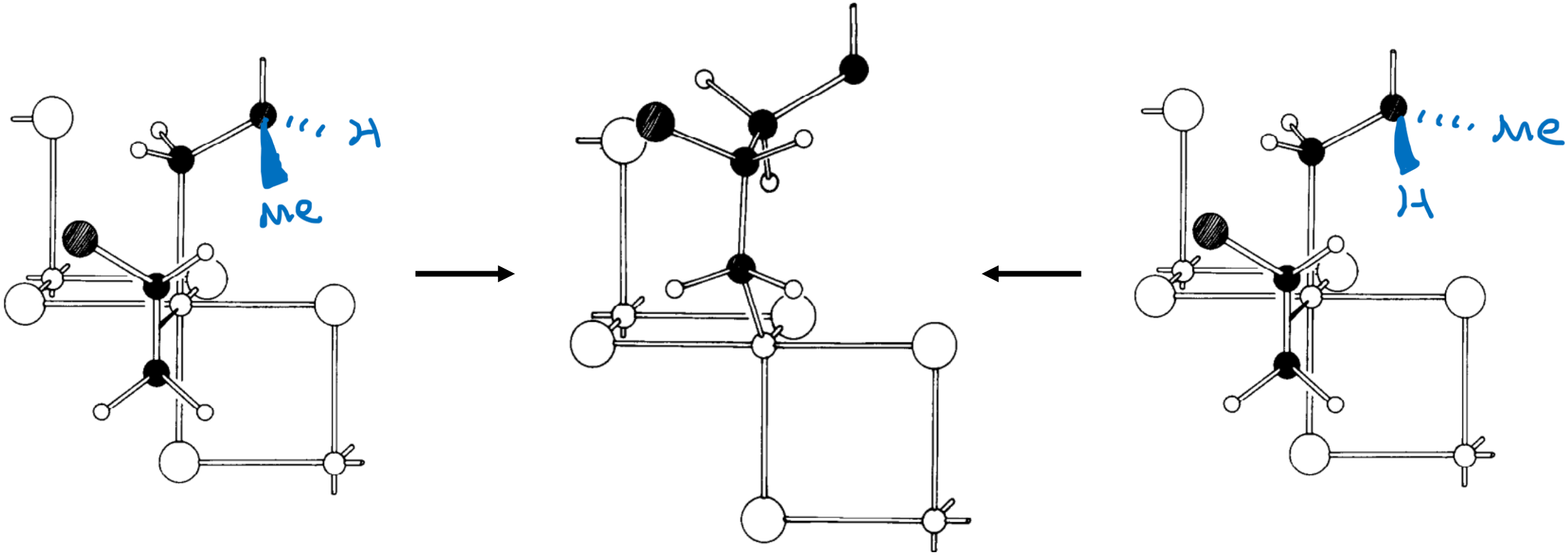
After primary insertion

Corradini, P.; Barone, V.; Fusco, R.; Guerra, G., *J. Catal.* **1982,** *77*, 32-42.

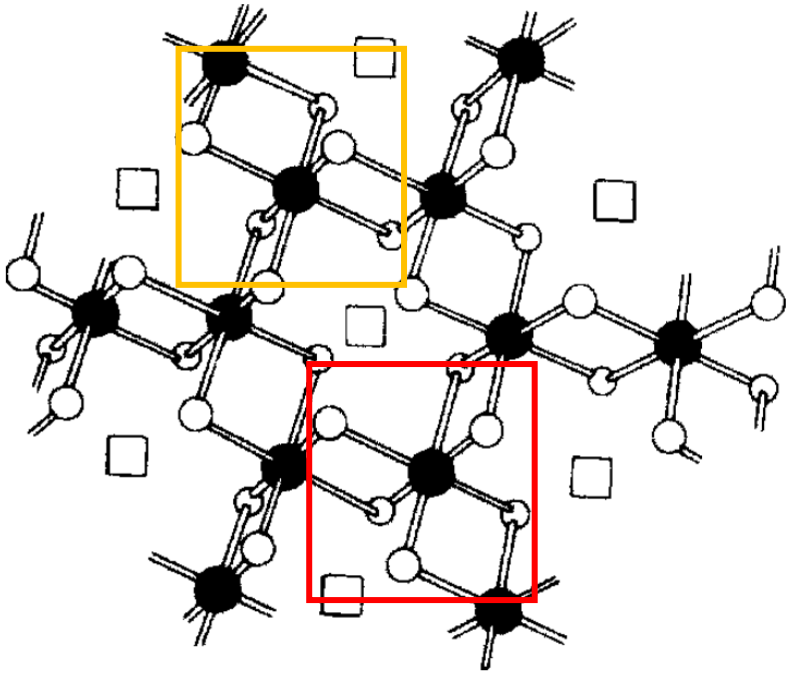
Catalyst Site Control

Catalyst (or enantiomorphic) site control:

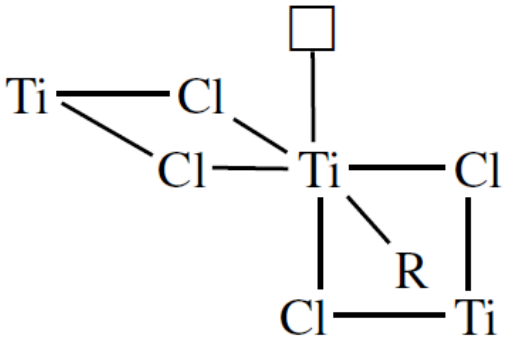
- Stereocontrol is achieved through the chiral environment established by the active initiator site.
- The structure of the propagating chain end does not influence the formation of the newly generated stereogenic center.

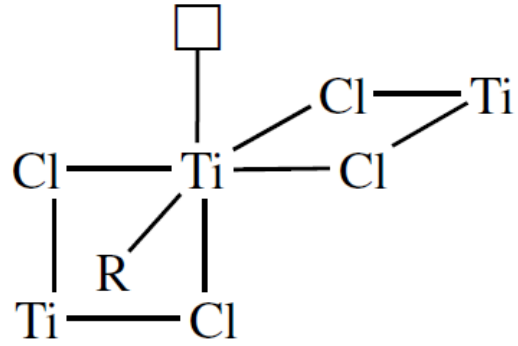


Catalyst Site Control

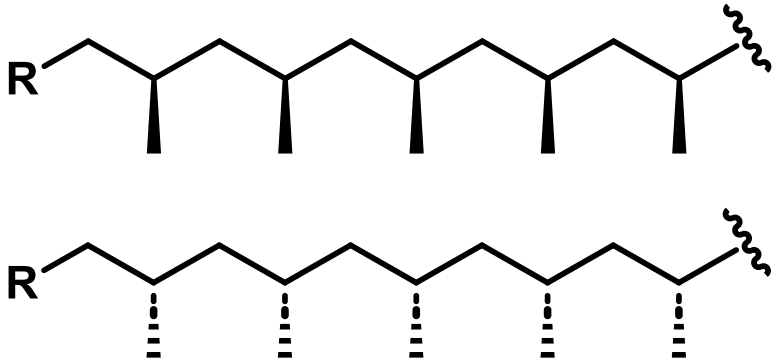


The two square Ti centers in the crystal of α-$TiCl_3$ are mirror images (enantiomers) of each other.





Each yields isotactic polymer molecules through nearly exclusive coordination with the *re* and *si* monomer enantioface, respectively.

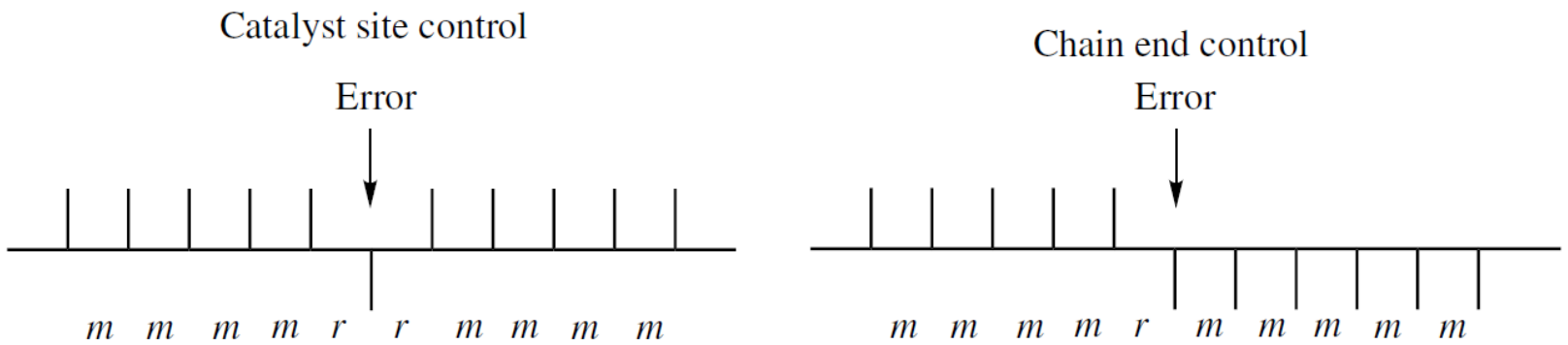


- Both enantiomeric sites produce isotactic polymers.
- The stereogenic centers in polymers are often “pseudochiral,” so the polymers produced by the two enantiomeric sites are virtually identical.

Polymer Chain End Control vs Catalyst Site Control

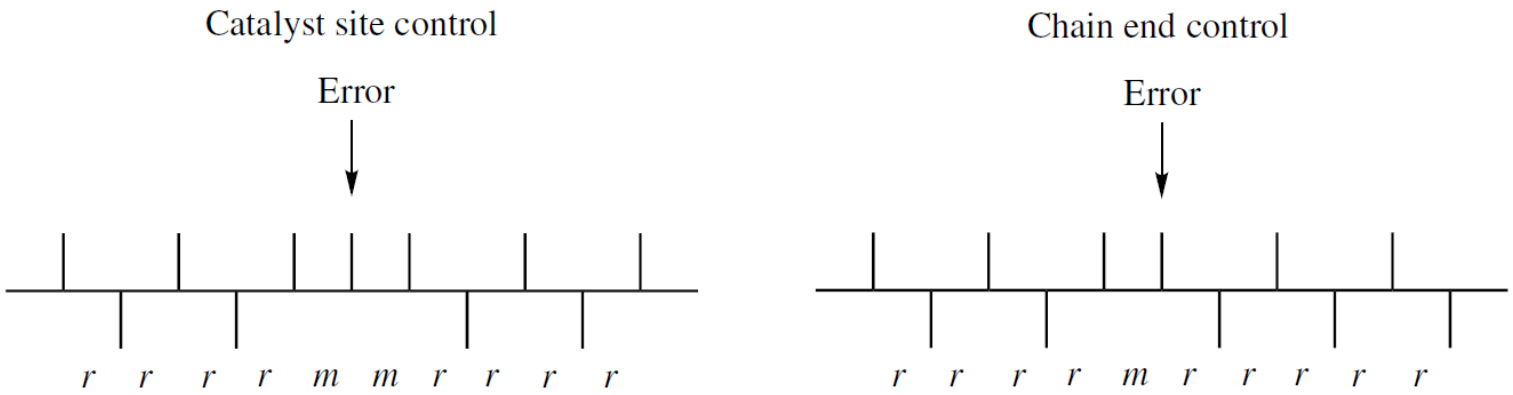
For two hypothetical isoselective polymerizations, one controlled by the catalyst site and the other by the polymer chain end:

Isoselective Polymerization

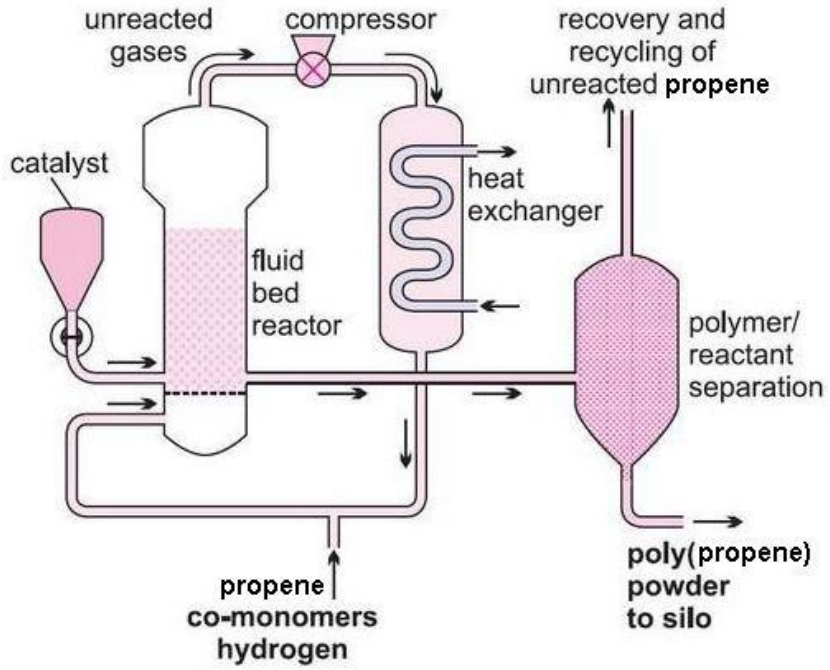


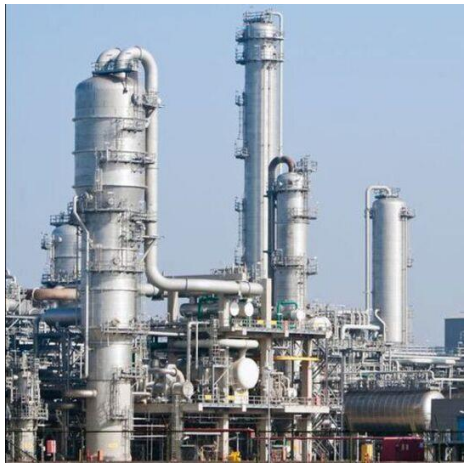
For two hypothetical syndioselective polymerizations, one controlled by the catalyst site and the other by the polymer chain end:

Syndioselective Polymerization



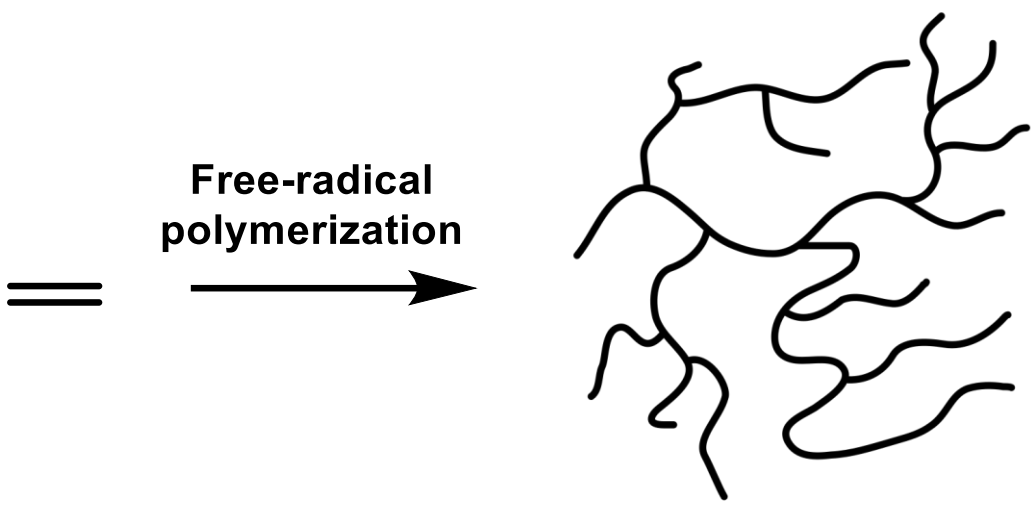
Application of Ziegler–Natta Catalyst: Polypropylene (PP)



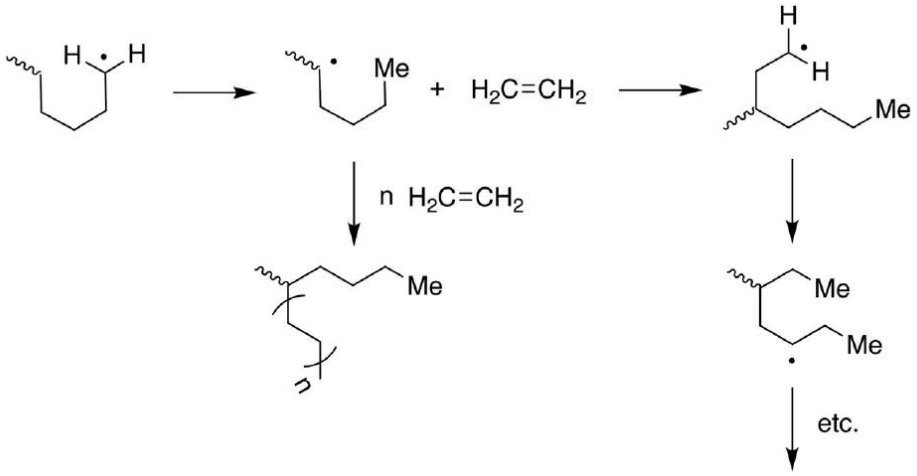


- Hydrogen is often used to control molecular weight, with commercial polypropylene (PP) typically in the range of 100,000 to 600,000 Da.
- The Ziegler–Natta catalyst produces PP with high dispersity (ranging from 5 to 30). For more information on the kinetics, refer to pages 658 to 664 in Odian.
- Isotactic PP is semi-crystalline and the second-most widely produced commodity plastic.

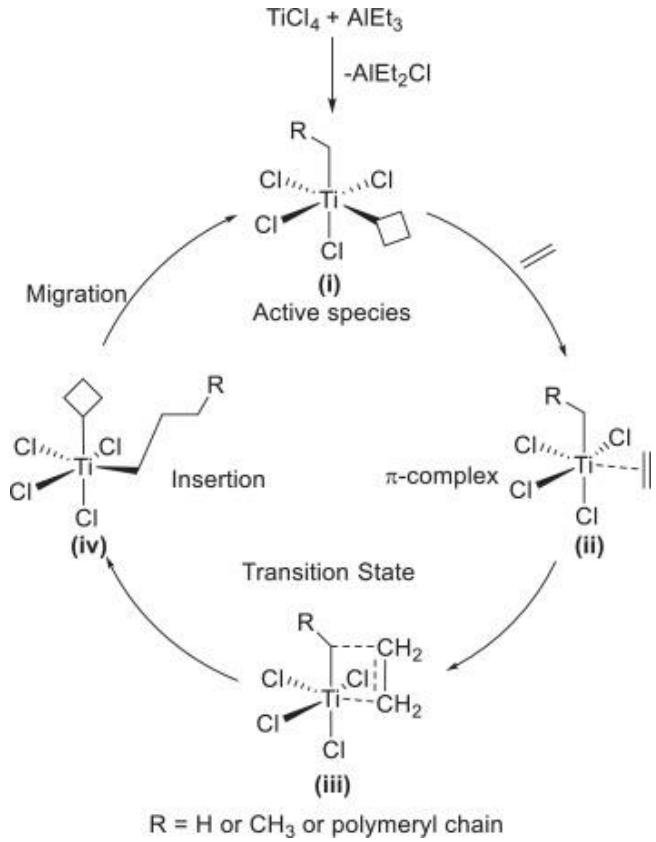
Application of Ziegler–Natta Catalyst: High-Density Polyethylene (HDPE)

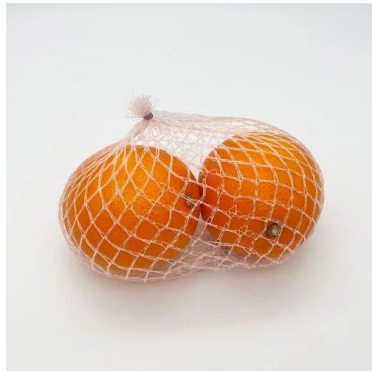


Low-density polyethylene (LDPE): highly branched



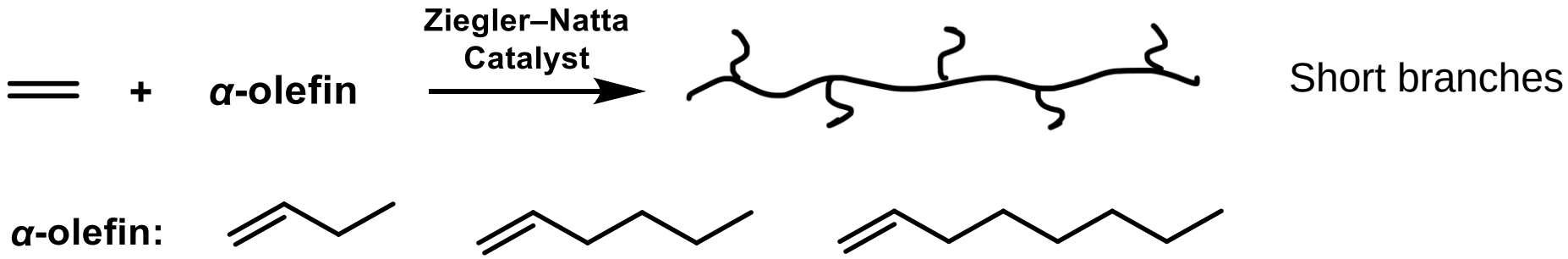
High-density polyethylene (HDPE): linear chain



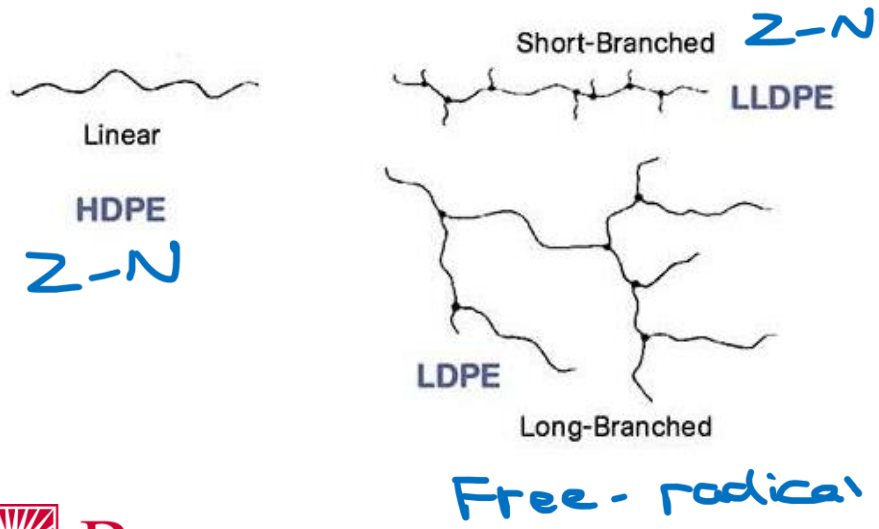


The better chain packing in HDPE results in higher crystallinity compared to LDPE (70–90% vs. 40–60%) and improved mechanical strength.

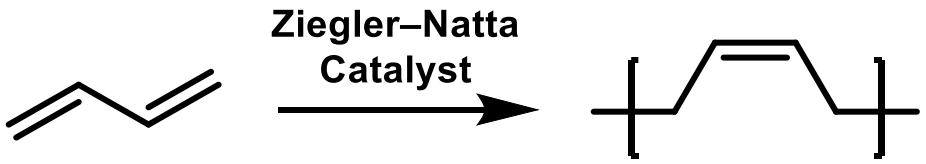
Application of Ziegler–Natta Catalyst: Linear Low-Density Polyethylene (LLDPE)



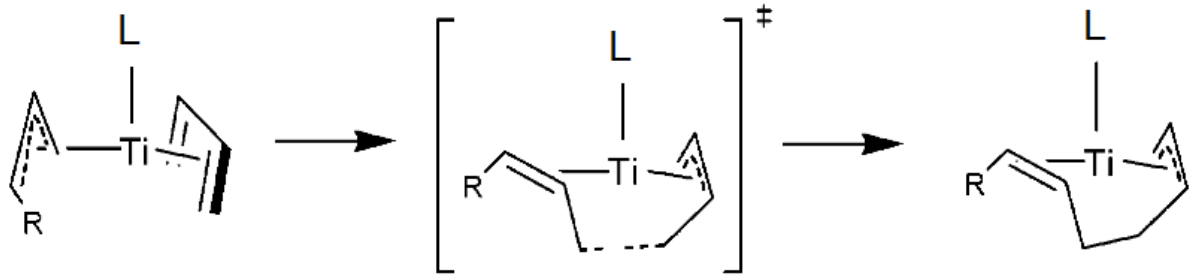
- LLDPE has comparable flexibility to LDPE but higher tensile strength.
- It has penetrated almost all traditional polyethylene markets, particularly those dominated by LDPE, and its production now exceeds that of LDPE.



Application of Ziegler–Natta Catalyst: *cis*-1,4-poly(1,3-butadiene)



cis-1,4-poly(1,3-butadiene)



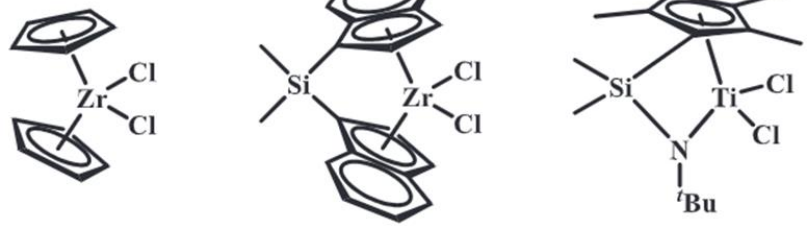
- Widely used in the tire industry, it is almost always combined with styrene-butadiene rubber (SBR) and natural rubber.
- Used as a starting material to synthesize acrylonitrile butadiene styrene (ABS).

Single-Site Catalysts

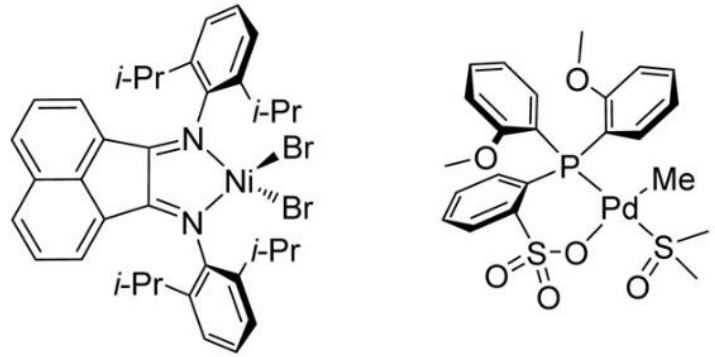
The Ziegler–Natta catalyst is perhaps one of the most relevant catalytic processes to everyday life. However, it is a heterogeneous catalytic system, where the active sites are non-uniform and structurally poorly defined. This results in several limitations:

- The reaction efficiency is highly dependent on how the catalysts ($TiCl_4$, $Al(C_2H_5)_3$, and $MgCl_2$) are mixed.
- It leads to a broad molecular weight distribution.
- Gaining mechanistic insights into the reaction is challenging.
- There is limited room for modulation or improvement (e.g., how to synthesize syndiotactic polypropylene).

Homogeneous single-site catalysts may overcome these limitations

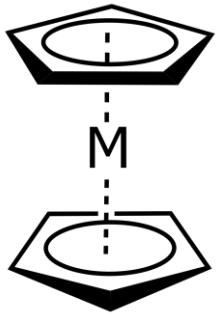


Early transition metals (Ti, Zr)



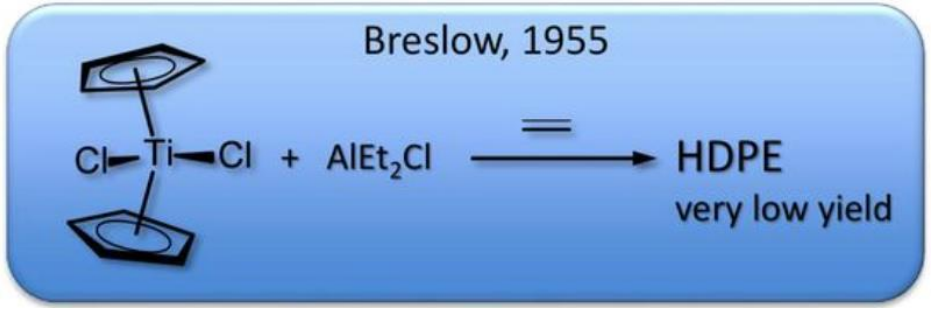
Late transition metals (Ni, Pd)

Early Metallocene Catalysis



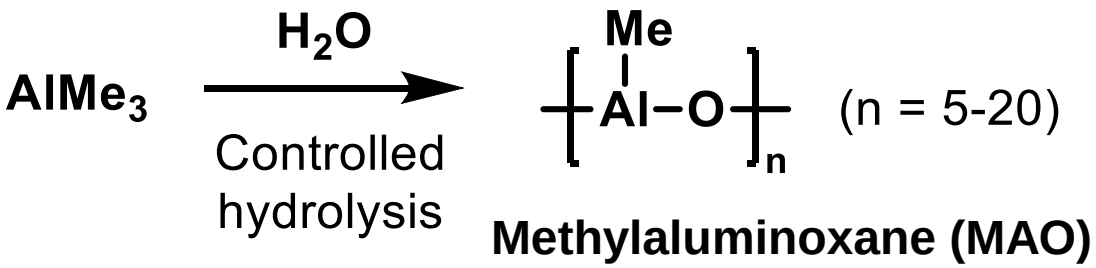
Cyclopentadienyl ($C_5H_5^-$, Cp)

Metallocene

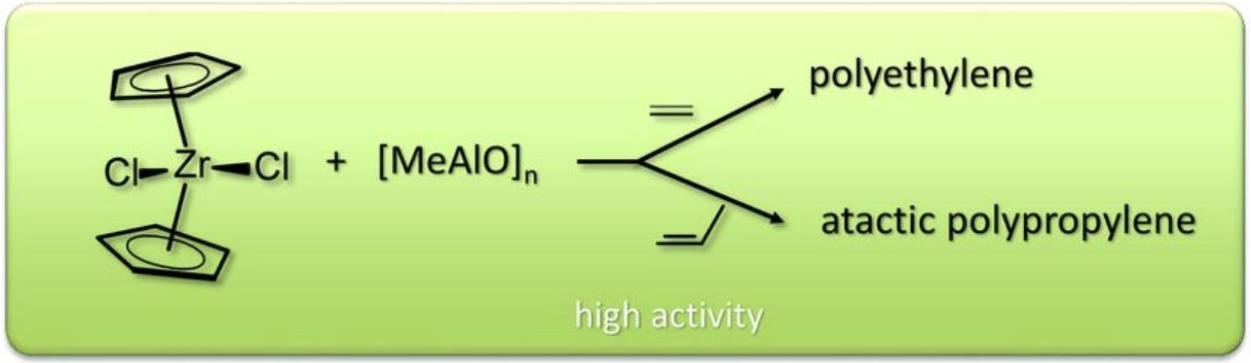


- Limited activity
- Propene: only dimerization
- Active species unclear

Breslow later (1975) discovered that the activity of titanocene is increased with the addition of water.

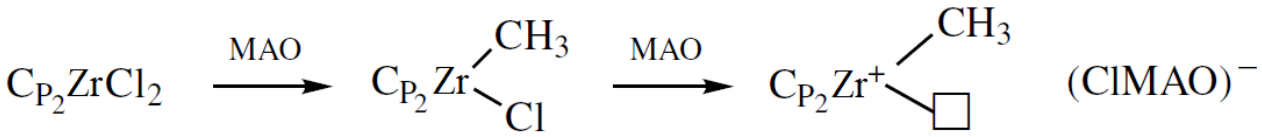


Methylaluminoxane (MAO)

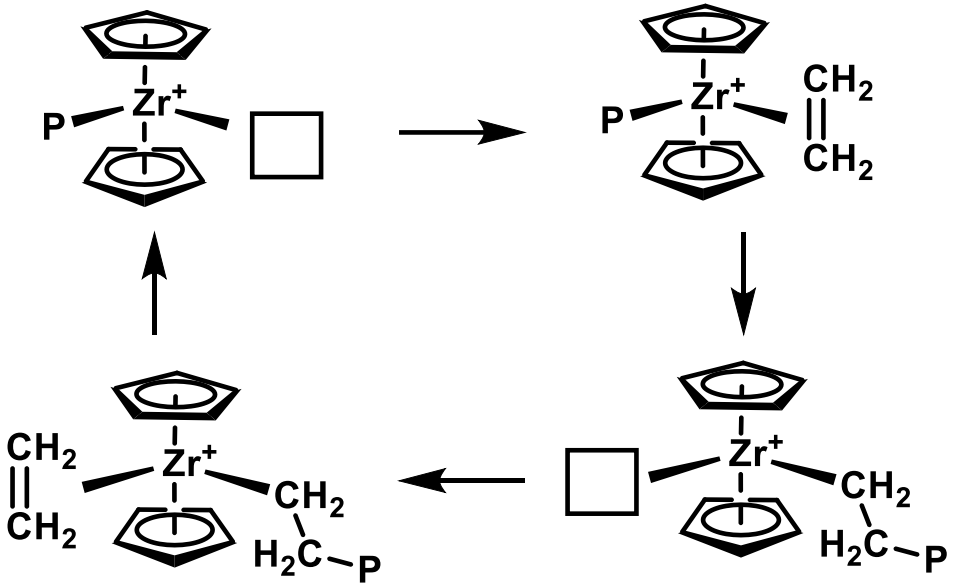


Kaminsky, 1980

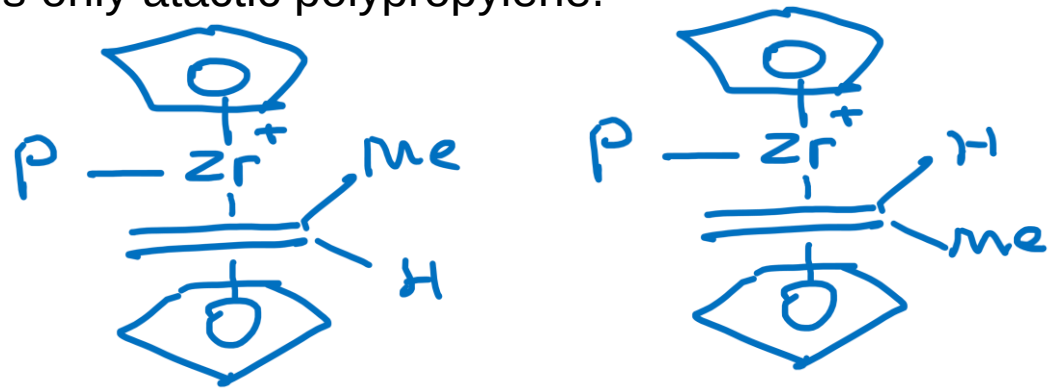
Mechanism of Polymerization with Metallocene



The reactivity is high because the counter-anion $(ClMAO)^-$ is a weakly coordinating anion.



This catalytic system polymerizes propylene with very high activity but yields only atactic polypropylene.

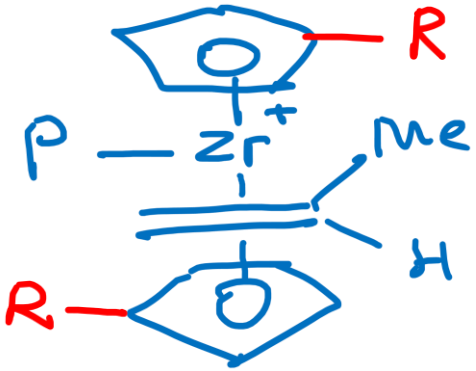


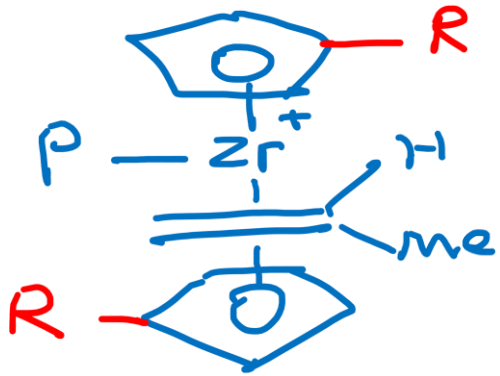
The coordination sites of these simple metallocene catalysts are not enantioselective and cannot distinguish between the prochiral faces of propylene.

"Windshield wiper" mechanism: the growing polymer chain flips back and forth between two coordination sites on the catalyst, somewhat like the movement of a car's windshield wiper.

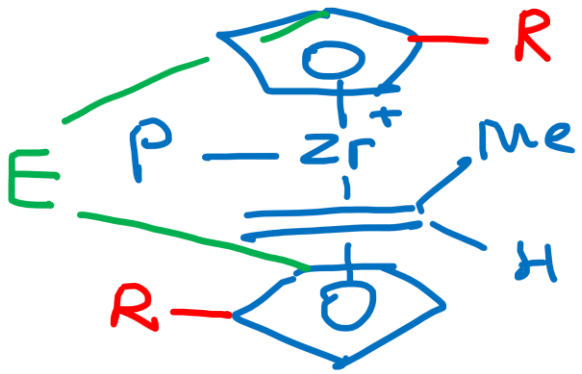
Stereoselective Metallocene Catalysts

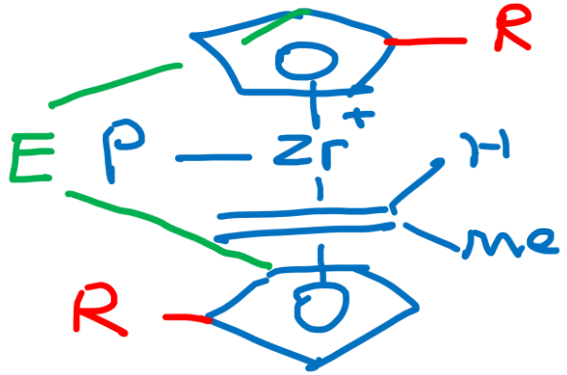
How can metallocene catalysts be designed to distinguish between the prochiral faces of propylene?



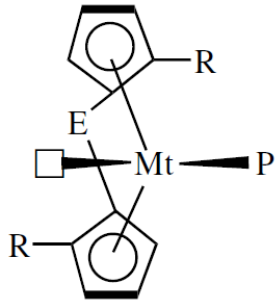


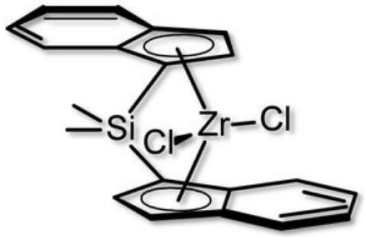
Introducing substituents on the cyclopentadienyl rings may make the two arrangements energetically different. However, the free rotation of these rings could counteract our efforts, so further locking of the cyclopentadienyl rings is necessary.





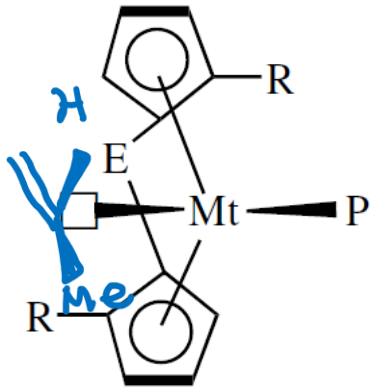
Isoselective Metallocene Catalysts

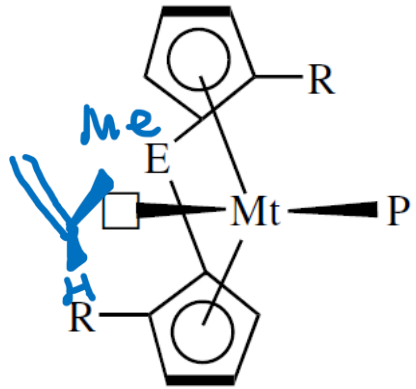




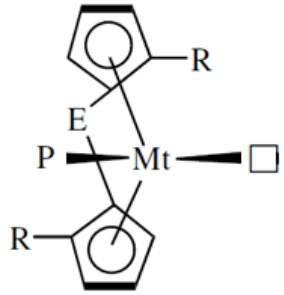
Q1: Are the coordination sites enantioselective?

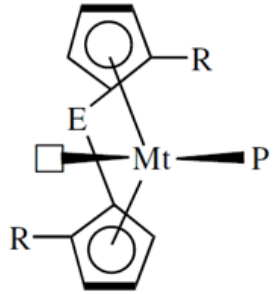
Yes





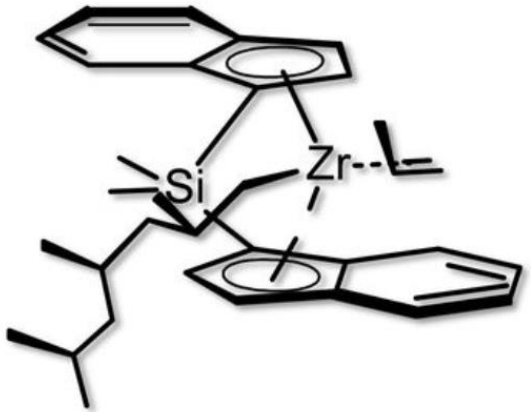
Q2: Are the two coordination sites homotopic or enantiotopic?

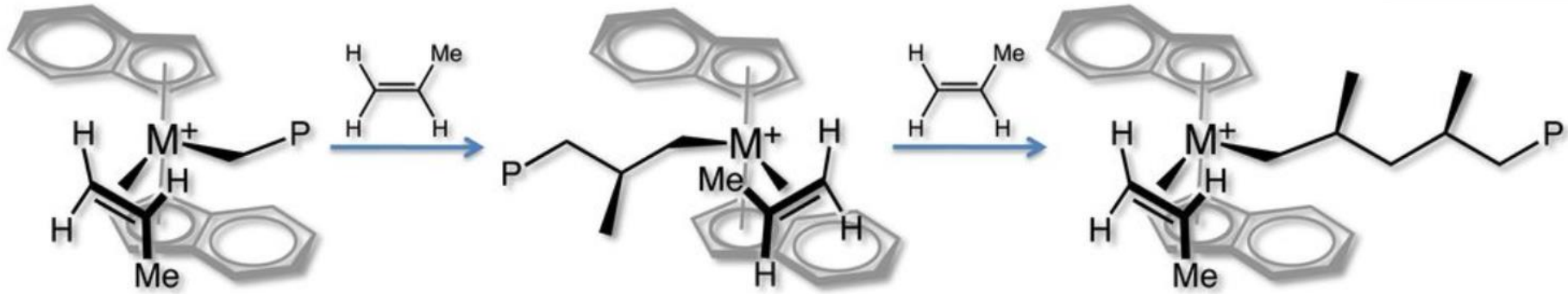




Switching the growing polymer and coordination sites leads to identical structures, indicating that they are homotopic.

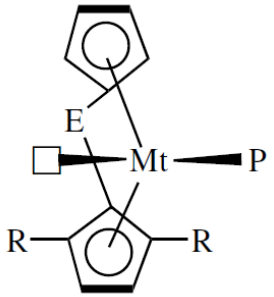
The two coordination sites exhibit identical enantioselectivity, which should result in an isotactic polymer.

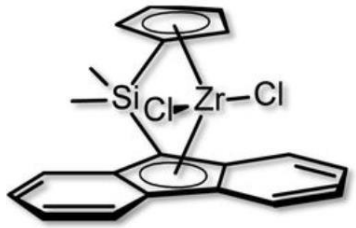




Catalyst Site Control

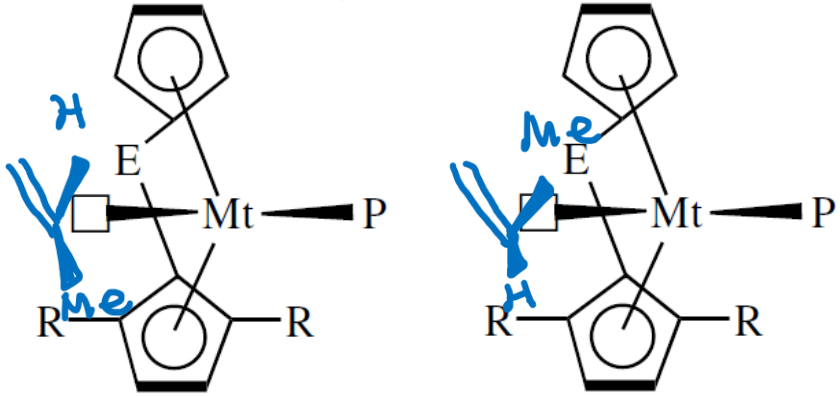
Syndioselective Metallocene Catalysts



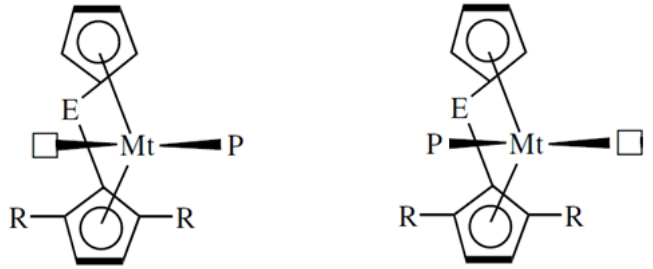


Q1: Are the coordination sites enantioselective?

Yes

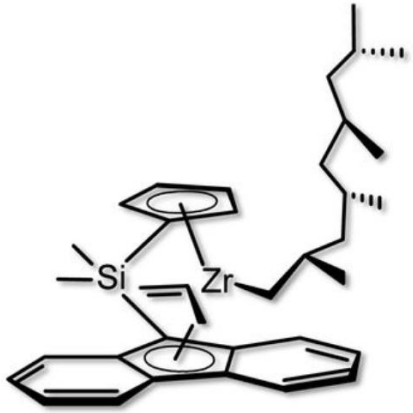


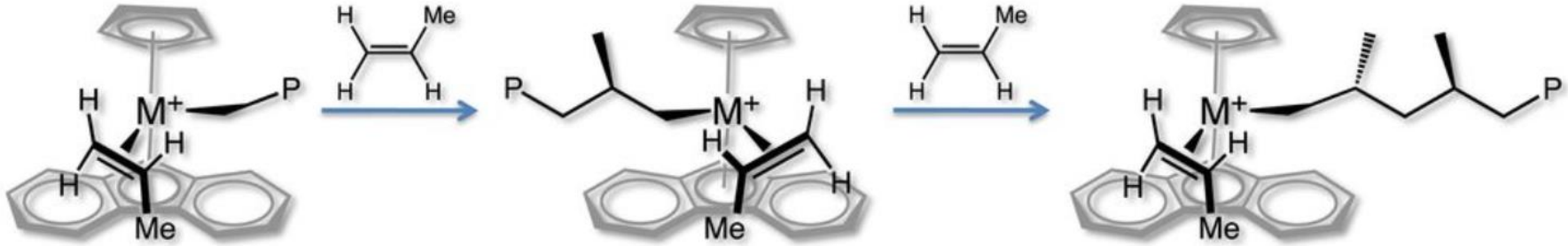
Q2: Are the two coordination sites homotopic or enantiotopic?



Switching the growing polymer and coordination sites leads to mirror images, indicating that they are enantiotopic.

The two coordination sites exhibit opposite enantioselectivity, which should result in an syndiotactic polymer.



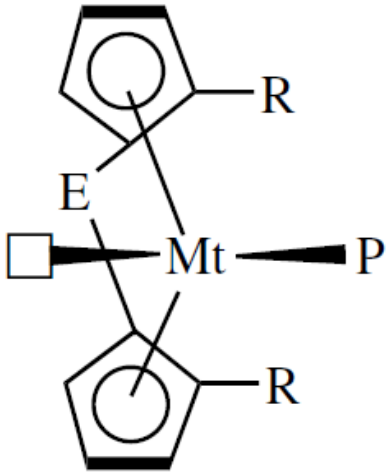


syndiospecific

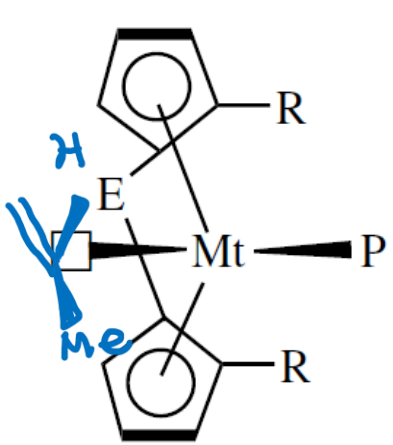
syndiospecific

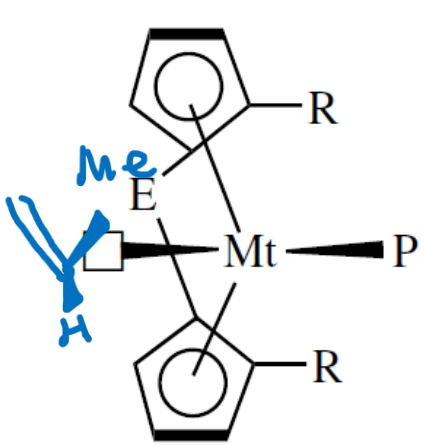
syndiospecific

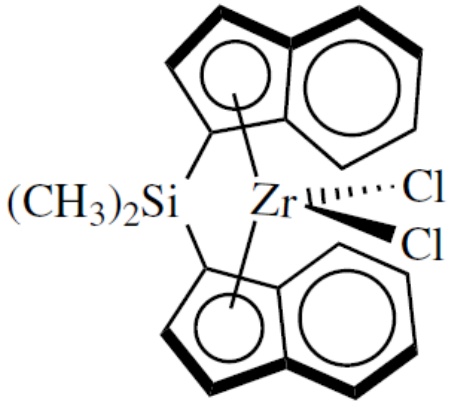
Non-Stereoselective Metallocene Catalysts

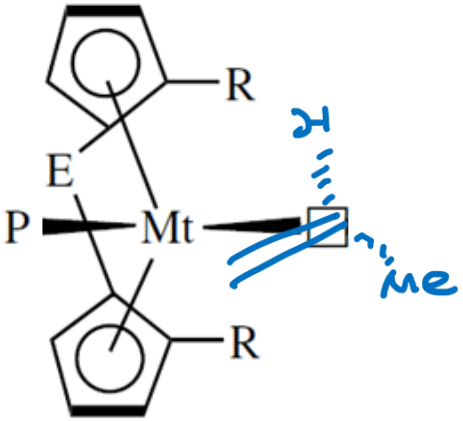


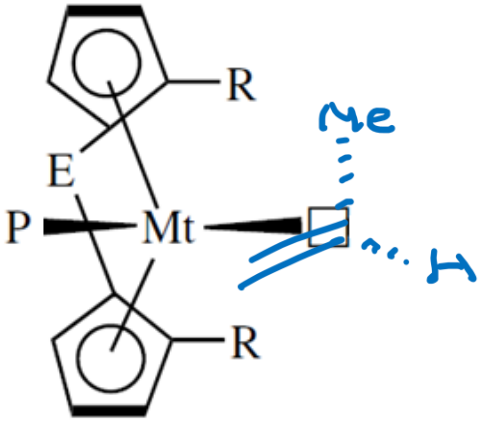
Q1: Are the coordination sites enantioselective?









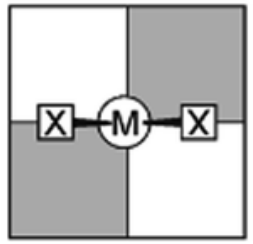


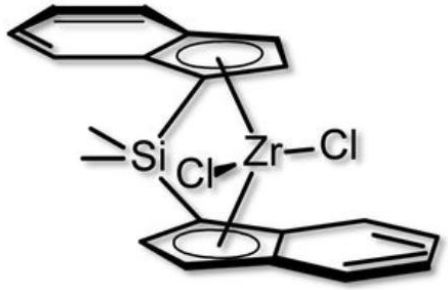
Both coordination sites are not enantioselective, so it results in an atactic polymer.

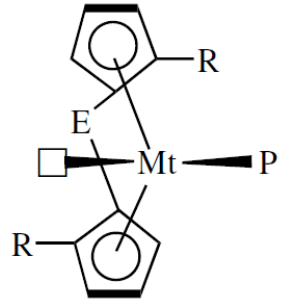
Summary of Metallocene Catalysts

Isotactic polymer

C_2-symmetric, chiral
Homotopic sites

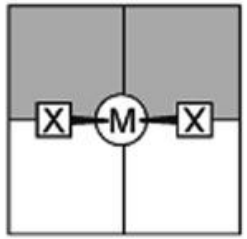


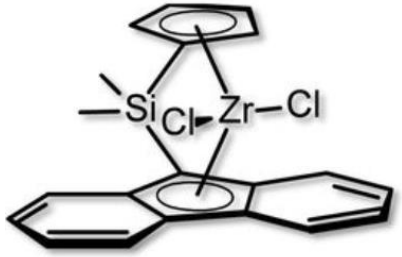


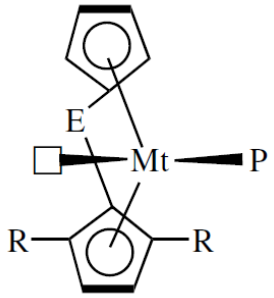


Syndiotactic polymer

C_S-symmetric, prochiral
Enantiotopic sites

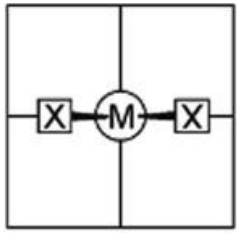


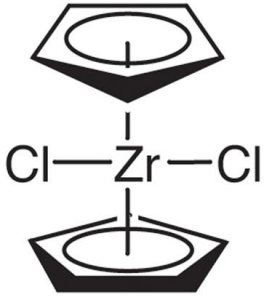


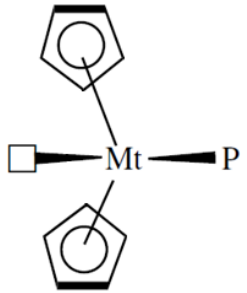


Atactic polymer

C_{2V}-symmetric, achiral
Homotopic sites

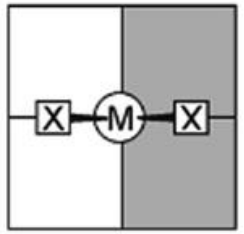


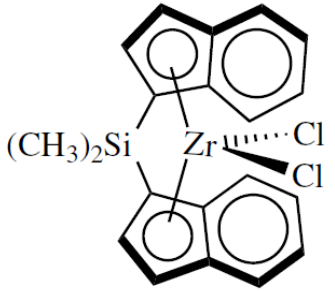


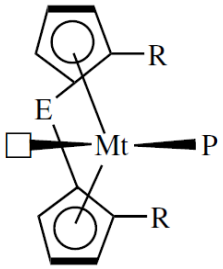


Atactic polymer

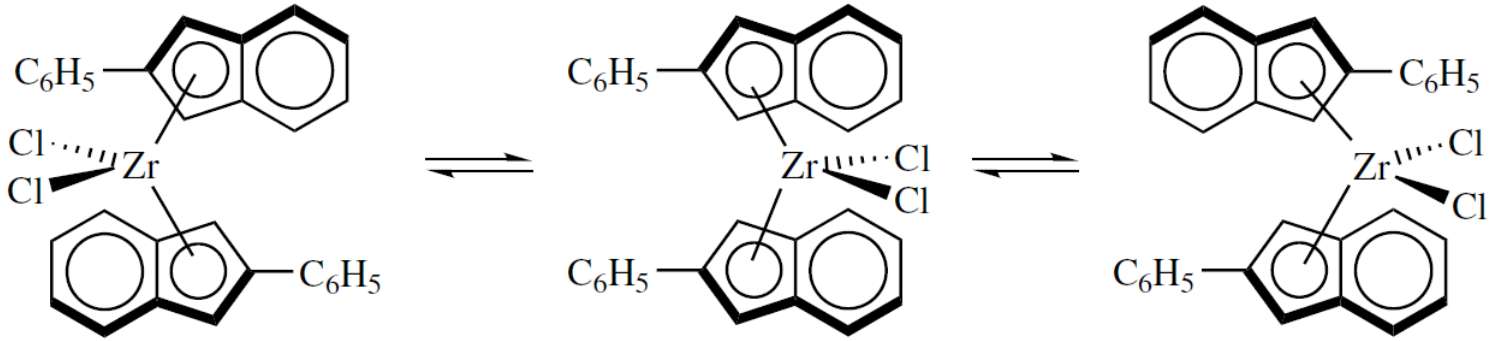
C_S-symmetric, achiral
Diastereotopic sites





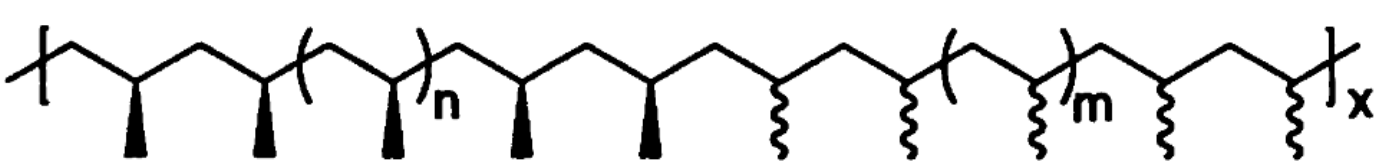


Oscillating Metallocenes



Isoselective Non-stereoselective Isoselective

The catalyst oscillates between isoselective and non-stereoselective states during polymerization, resulting in isotactic-atactic stereoblock copolymers.



Isotactic-atactic stereoblock

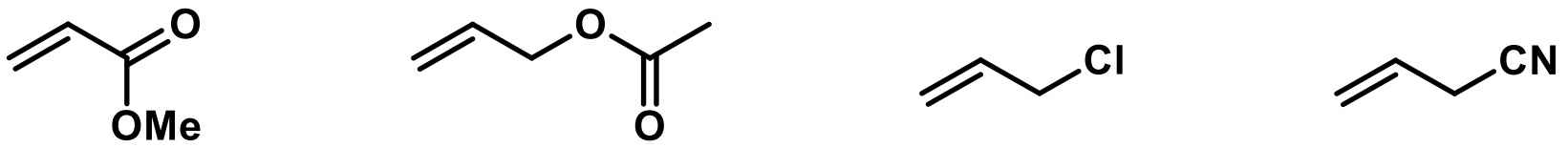
Why is this useful?

Isotactic PP is crystalline, while atactic PP is amorphous, so we obtain a thermoplastic elastomer from a single feedstock (propylene)!

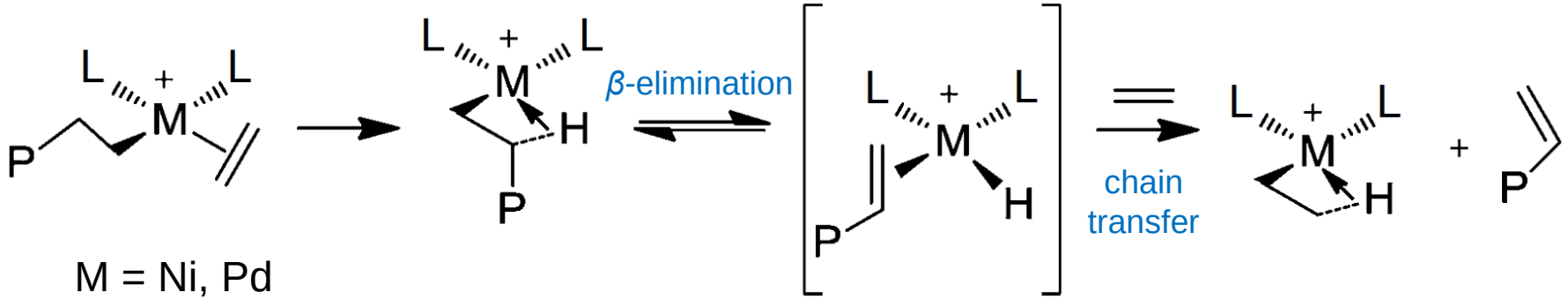
Coates, G. W.; Waymouth, R. M., *Science* **1995,** *267*, 217-219.

Late Transition Metal Catalysts

- Incorporation of polar comonomers into polyolefins is often highly desirable to modulate their properties and increase their compatibility with a wider range of polymers used in industry.



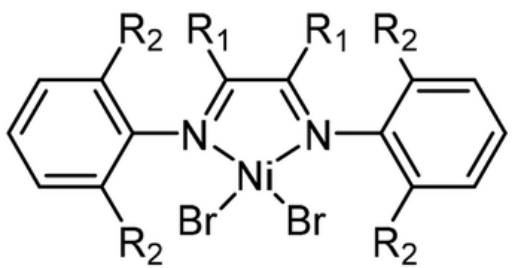
- However, early transition metallocenes (Zr, Ti, Hf) are highly oxophilic and thus intolerant of polar comonomers. Even a small amount of such comonomers can irreversibly coordinate with the early transition metal centers and completely deactivate the catalysts.
- Considering the structural similarity between some cationic late transition metal catalysts and the active species involved in metallocene catalysts, it was postulated that such catalysts might enable the copolymerization of olefins and polar monomers due to their lower oxyphilicity. However, late transition metal complexes are much more prone to *β*-elimination, resulting in rapid chain transfer.



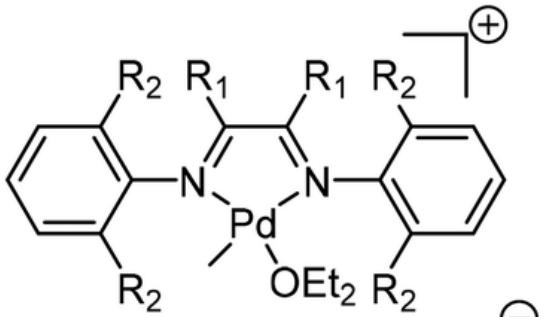
M = Ni, Pd

The Brookhart Catalysts

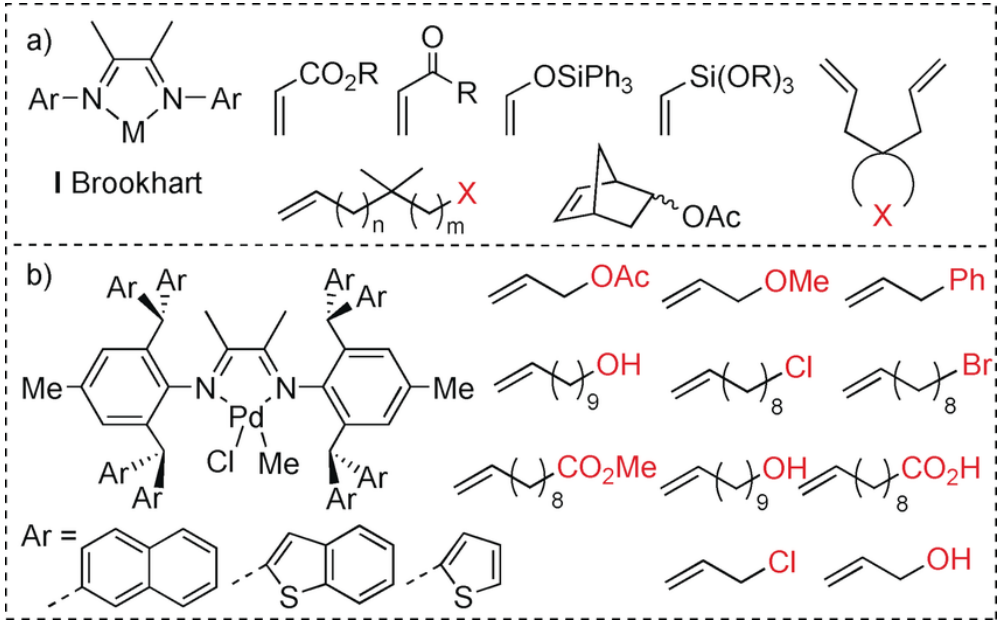
In 1995, Brookhart found that the use of bulky *α*-diimine ligands significantly suppressed chain transfer, leading to the polymerization of ethylene into polymers with molecular weights of 10^4–10^6.



C1a R_1 = H, Me, An;
R_2 = H, Me, ^{i}Pr, etc



C1b R_1 = H, Me; BAr'_4
R_2 = H, Me, ^{i}Pr, etc

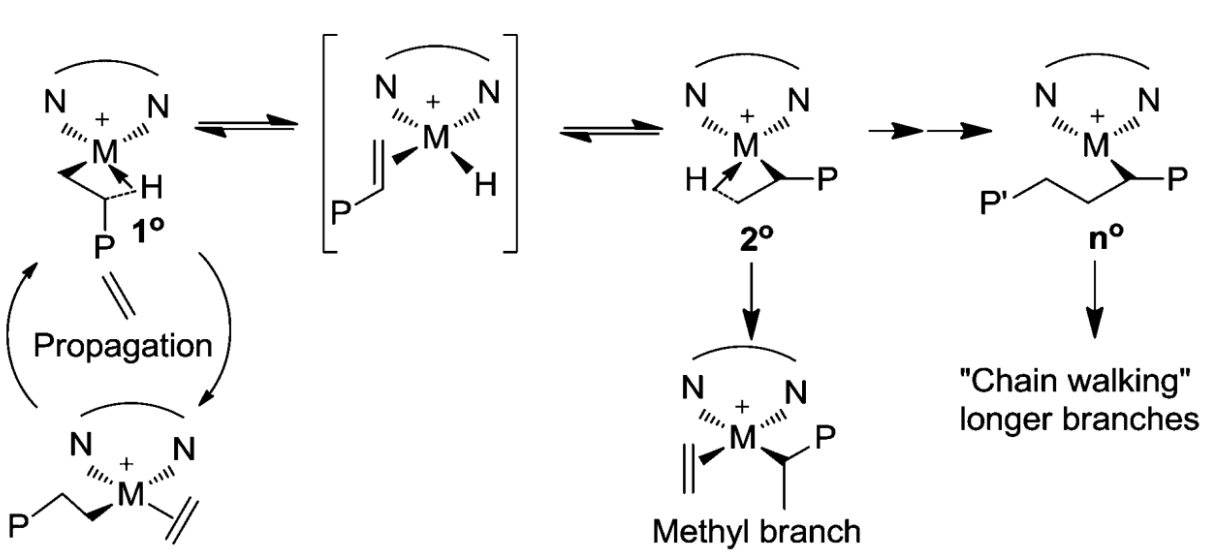


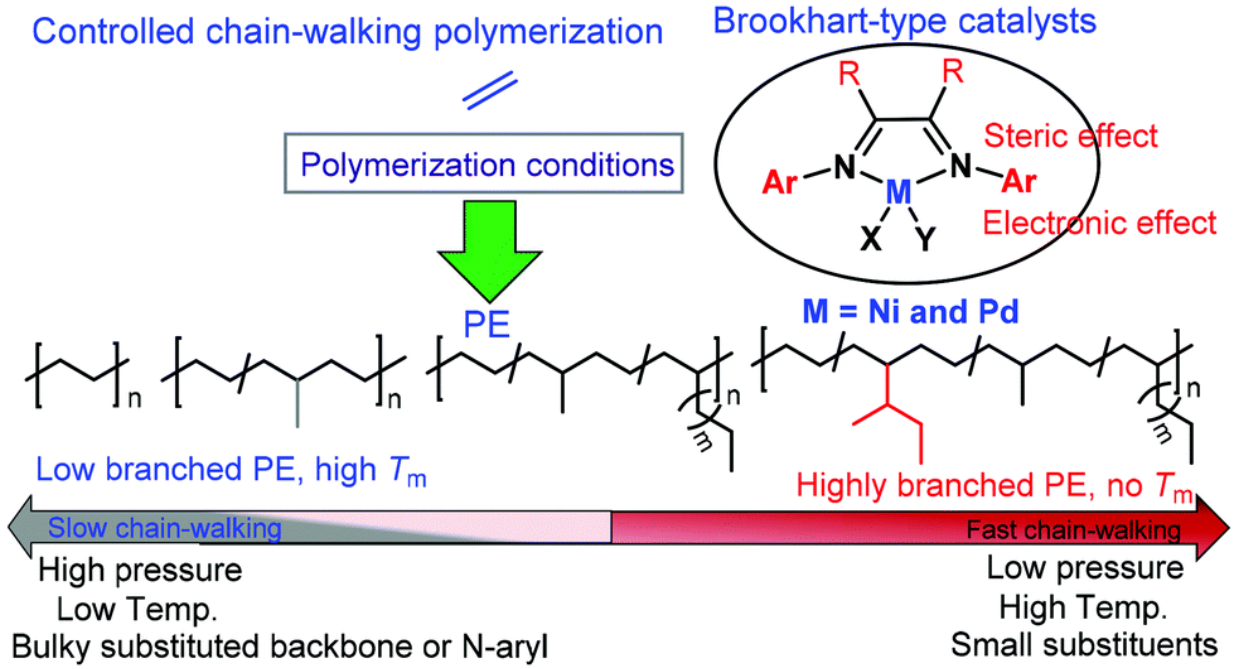
- Compared to early transition metal catalysts (e.g., Ziegler-Natta, metallocenes), Brookhart catalysts exhibit significant secondary insertion (i.e., poorer regioselectivity) and do not demonstrate high stereoselectivity in the polymerization of *α*-olefins such as propylene.
- However, Brookhart catalysts show decent tolerance to polar monomers and allow the copolymerization of ethylene with polar monomers such as methyl acrylate.

Johnson, L. K.; Killian, C. M.; Brookhart, M., *J. Am. Chem. Soc.* **1995,** *117*, 6414-6415.

The Brookhart Catalysts

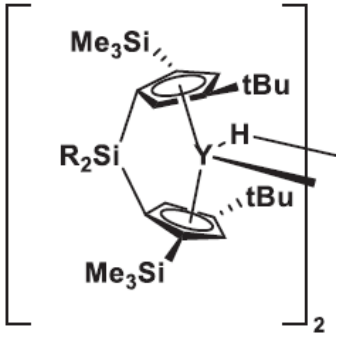
β-Elimination occurs extensively with Brookhart catalysts, leading to a process called “chain-walking”, which produces highly branched or even hyperbranched polyolefins (much more highly branched even than LDPE).



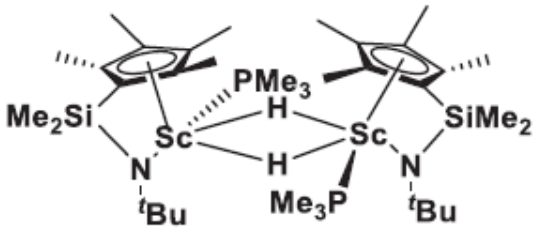


Wang, F.; Chen, C., *Polym. Chem.* **2019,** *10*, 2354-2369.

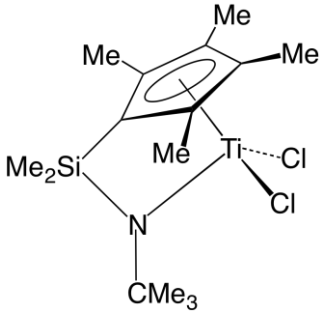
Other Examples of Post-Metallocene Catalysts



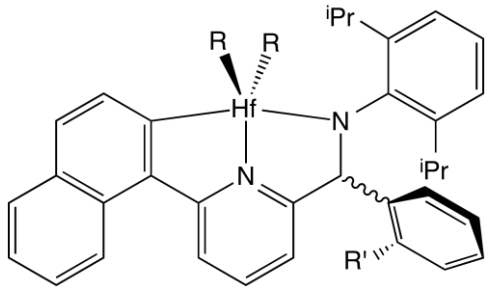
Marks (1985)



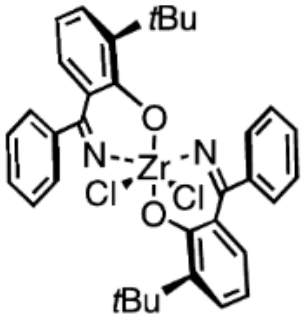
Constrained geometry complex
Bercow (1990)



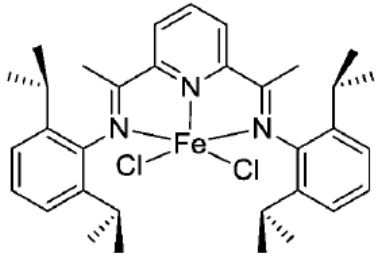
Constrained geometry complex
Dow (1991)



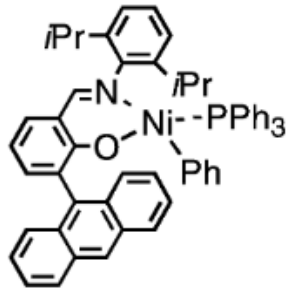
Pyridylamide - Dow (2003)



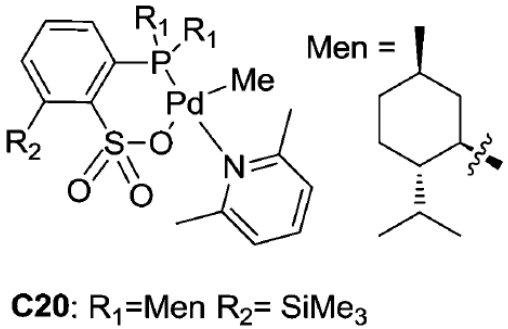
Phenoxy-imine (FI)
Fujita (1998)



Bis(arylimino)pyridyl Fe (II)
Gibson, Brookhart (1998)



Salicylaldiminato
Grubbs (2000)



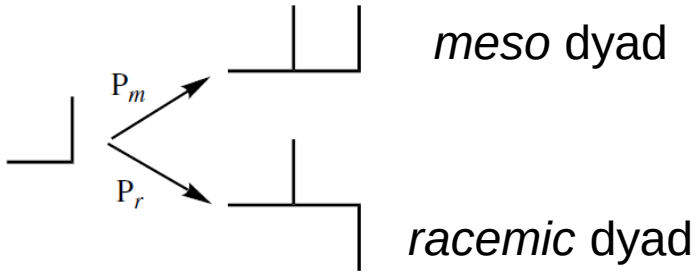
Phosphine-sulfonate
Nozaki (2016)

The development of homogeneous single-site catalysts has provided key mechanistic insights into olefin polymerization. While Ziegler-Natta-based heterogeneous catalysts still dominate the polymer industry, more homogeneous single-site catalysts are now used for production of specialty polyolefins.

Statistical Models of Propagation

Polymer Chain End Control

Assumption: only the last monomer unit in the propagating chain end is important in determining polymer stereochemistry.



meso dyad

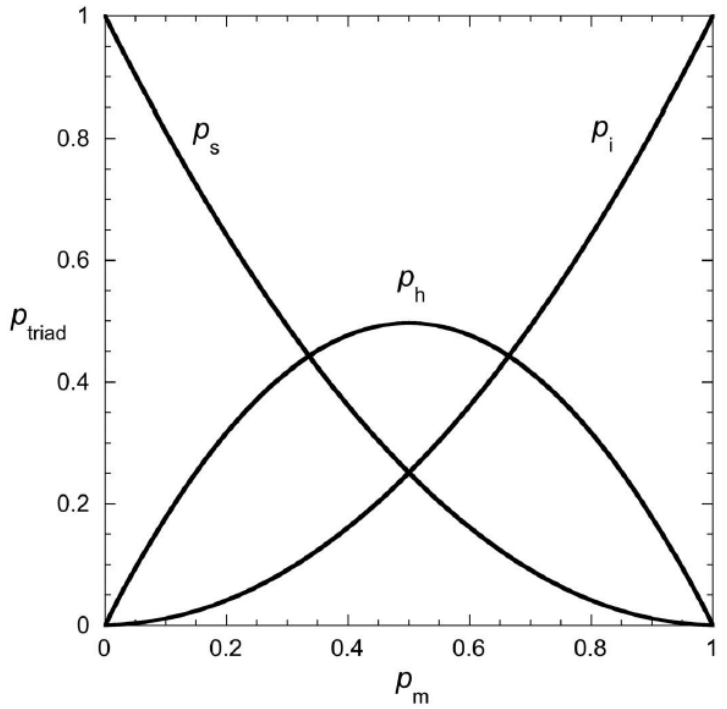
racemic dyad

A simple statistic applies (zero-order Markov model)

P_i: $(mm) = P_m^2$

P_h: $(mr) = 2P_m(1 - P_m)$

P_s: $(rr) = (1 - P_m)^2$



- Triads can be quantified using NMR. By testing whether their ratio follows the statistics described above, one can determine whether the stereochemistry of the polymerization results from simple chain end control.
- It is also possible for a polymerization where the penultimate unit plays a crucial role in determining subsequent stereochemistry. The statistics of such processes can be described by a first-order Markov model (see Page 709 in Odian for details; it is actually quite similar to the copolymerization statistics we discussed in Lecture 8).

Statistical Models of Propagation

Catalyst Site Control

- Consider the Ziegler-Natta catalyst, which has two enantiomeric growing sites: the "R" site that recognizes the *re* face of propylene, and the "S" site that recognizes the *si* face. Since the same statistics apply to both sites, we will focus on the "R" site. The statistical model requires only one parameter, σ, the probability of an *re* monomer unit adding at the "R" site. Thus, 1 - σ represents the probability of an *si* monomer unit adding at the "R" site. (i.e., 1 - σ reflects the likelihood of catalyst errors.)

- The dyad fractions are given by:

$(m) = \sigma^2 + (1-\sigma)^2$ *meso* dyad: the two subsequent additions need to be either both “right” or both “wrong”.

$(r) = 2\sigma(1-\sigma)$ *racemic* dyad: the two subsequent additions need to be one “right” and one “wrong”.

- The triad fractions are given by

$(mm) = 1 - 3\sigma(1-\sigma)$ RRR or WWW $\sigma^3 + (1-\sigma)^3 = 1 - 3\sigma + 3\sigma^2$

$(mr) = 2\sigma(1-\sigma)$ $1 - (mm) - (rr) = 1 - (1 - 3\sigma + 3\sigma^2) - (\sigma - \sigma^2) = 2\sigma - 2\sigma^2$

$(rr) = \sigma(1-\sigma)$ RWR or WRW $\sigma^2(1-\sigma) + (1-\sigma)^2\sigma = \sigma - \sigma^2$

By determining the triad distribution using NMR and comparing it with the statistics described above, one can determine whether the stereochemistry of the polymerization results from catalyst site control.