Mechanism, Stereochemistry and Applications of Homogeneous Ziegler-Natta Polymerization

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Poly-Olefins in Industry and Society

Poly-olefins
- Fastest-growing segment of the polymer industry
- World-wide production is in excess of 160 billion pounds/year

The three major classes of polyethylene:
- High density polyethylene (HDPE) is a linear, semi-crystalline homopolymer of ethene
- Linear low-density polyethylene (LLDPE) is a random copolymer of ethylene and alpha-olefins
- Low density polyethylene (LDPE) is a branched ethylene homopolymer

Uses of Poly-olefins
- Vary from asphalt blends and sealants (amorphous) to surgical prostheses (Linear, Ultra-HDPE)
Polymer Properties

- Polymer tacticities, connectivities, and lengths

### Connectivity

**Regio-irregular**

**Regio-regular**

### Stereochemistry

**Isotactic**

**Syndiotactic (antiotactic)**

**Isotactic-Atactic Stereo-block**

**Atactic**

### Degree of Polymerization

- Goal of modern polymer chemistry is to control all factors of a polymers microscopic structure
Historical Work of Ziegler and Natta

- Early polymerization w/ aluminum: The “Aufbaureaktion”

\[
\text{Al}(\text{Et})_3 + \text{H}_2\text{C}=\text{CH}_2 \xrightarrow{(100 \text{ atm.}) \: 100 \, ^\circ\text{C}} \quad \text{Al}(\text{C}_2\text{H}_4)_m\text{C}_2\text{H}_5 \xrightarrow{\text{O}_2, \text{H}_2\text{O}} \quad \text{HO}-(\text{C}_2\text{H}_4)_m\text{C}_2\text{H}_5
\]

\[
\text{m,n,o} < 100
\]

- Large scale production of detergents


- Polymerization of ethylene

\[
\text{H}_2\text{C}=\text{CH}_2 \xrightarrow{\text{EtAlCl/TiCl}_4 \: 1-5 \text{ atm, } 23 - 60 \, ^\circ\text{C}} \quad \begin{array}{c}\text{n} \\
\text{high molecular weight, Linear PE} \\
\text{low pressures and temperatures}
\end{array}
\]

Natta’s Contribution

\[
\text{EtAlCl/VCl}_4 \xrightarrow{1-5 \text{ atm, } 23 - 60 \, ^\circ\text{C}} \quad \begin{array}{c}\text{n} \\
\text{1st example of a crystalline isotactic polypropylene}
\end{array}
\]


Nobel Prize in Chemistry to Ziegler and Natta in 1963
Homogeneous Metalloocene Catalysts

- Synthesis of Ti(III) metalloocene/Al complex

\[
\begin{align*}
\text{Ti} \vdash \text{Cl} & \quad + \quad \text{Cl} \vdash \text{Al} \quad \xrightarrow{\text{Heptane}} \quad \text{Blue Crystalline Solid (Air Sensitive)} \\
\text{Ti} \vdash \text{Cl} & \quad + \quad \text{Cl} \vdash \text{Al} \quad \xrightarrow{\text{H}_2\text{C}=\text{CH}_2 (g) \ \text{w/} \ 0.025 \ \text{mol}\% \ \text{O}_2} \quad 1 \ \text{L Toluene, 15 °C, 1h}}
\end{align*}
\]

- Authors propose that oxygen oxidizes the Ti(III) to the active Ti(IV) catalyst
- Raises question of the role of the aluminum activator
- Earliest example of homogeneous metalloocene cat.

Breslow, D et. al. JACS, 1959, 81, 81.
Intermittent-Growth Model

- Kinetic studies of Reichert, Fink and Eisch
  - Kinetic studies on alkylaluminum activated metallocene catalysts revealed that polymer growth alternated b/w dormant and active states.
  - Lead to the development of the intermittent-growth model

\[ C^{*} \rightarrow P_{n-1} \quad \text{Al}_{2} \quad \text{Al}_{2}^{'} \quad C \rightarrow P_{n} \quad \text{Al}_{2} \quad \text{Al}_{2}^{'} \quad C \rightarrow P_{n+1} \quad \text{Al}_{2} = (\text{AlEtCl})_{2} \quad \text{Al}^{'} = (\text{unknown}) \quad P_{n} = \text{Polymer chain} \quad C = \text{Inactive state} \quad C^{*} = \text{Active state} \]

Activator-Free Polymerization

- Study by Jordan and co-workers

\[
\begin{align*}
\text{Zr} \cdot \text{Me} + \text{Ag[BPh}_4\text{]} & \quad \rightarrow \quad \text{Zr} \cdot \text{Me} + \text{Ag}^0 + \text{C}_2\text{H}_6 \\
80\% \text{ yield} & \quad \not\text{obs.}
\end{align*}
\]

- Activity towards polymerization of ethene

\[
\text{C}_2\text{H}_4 \text{ (4 atm.)} \quad \rightarrow \quad \text{[Cp}_2\text{Zr(Me)(THF)][AgBPh}_4\text{]} \quad \text{DCM, 23 °C, 1h} \quad \rightarrow \quad \text{n}\]

- Activity of ca. 0.2g/(mmol cat.)

- Reduced activity attributed to ligand exchange b/w ethene and THF

The Role of Water: MAO Activators

- Interesting observation by Kaminsky and Sinn

\[
\begin{align*}
\text{C}_2\text{H}_4 (7.9 \text{ atm}) \\
\text{H}_2\text{O} \\
\text{Toluene, } 21^\circ\text{C}
\end{align*}
\]

- Best activity observed for Al/H2O ratios of 2:1 to 5:1
- For Al/H2O ratio of 1/3 activity dramatically drops

Authors attributed increased activity to the formation of methyl aluminoxanes (MAO)

**MAO Activators** (The “Black-Box”) 

- Prepared by the control hydrolysis of trimethylaluminum
- Exact structure and composition are not well understood

1D linear or cyclic chains (3-coordinate Al)  
2D-cyclic structures (3- and 4-coordinate Al)  
3D-clusters (3- and 4-coordinate Al)

- Multiple equilibria present in solution further complicate matters

\[
\text{[Al(Me)O]}_n \cdot x \text{AlMe}_3 \rightleftharpoons \text{[Al(Me)O]}_n \cdot (x-y) \text{AlMe}_3 + y \text{AlMe}_3
\]

- Generally accepted that the mechanism of activation involves abstraction of a chloride (L₂ZrClMe) or a methyl anion (L₂ZrMe₂).
- Large excesses are needed (>200/1, Al/Ti)

“Cation-Like” Homogeneous Polymerization

- Study by Marks on “Cation-like” homogeneous Zr-Catalysts

\[ \text{Benzene} \quad \begin{array}{c} \text{Me} \\ \text{Me} \\ \text{Me} \end{array} \quad + \quad \text{B(C_6F_5)_3} \quad \rightarrow \quad \left[ \text{1,2-(CH}_3\text{)_2C}_5\text{H}_3\text{]}_2\text{ZrCH}_3^+ \ \text{CH}_3\text{B(C}_6\text{F}_5\text{)_3}^- \right] \]

Crystalline solid characterized by EA, MS, NMR and X-Ray

Key Distances:
- Zr-C(15): 2.273 Å (2.280 for Cp_2ZrMe_2)
- Zr-C(34): 2.549 Å (2.249 Å for other μ-CH_3)
- B-C(34): 1.663 Å (normal)
- Zr-H(B): 2.25 Å (2.16 Å for other agostic H's)

Key Angles:
- Zr-C(34)-B =161.8
- C(16)-B-C(34) = 108.7
- C(22)-B-C(34) = 112.7,
- C(28)-B-C(34) = 102.8
- C(16)-B-C(22) = 106.5
- C(16)-B-C(28) = 114.3
- C(22)-B-C(28) = 112.0.

- Highly unsymmetrical bridging methyl
- Shortened Zr-C(15) bond
- Boron distance/angles are typical

Marks, T. et. al. JACS, 1991, 113, 3623
“Cation-Like” Homogeneous Polymerization

- Polymerization of ethylene and propylene

\[
\begin{align*}
\text{H}_2\text{C}=&\text{CH}_2 \\
\text{Zr-Cat.} & \\
\text{Toluene, 23 °C, 0.5 h} & \\
\text{H}_2\text{C}=&\text{CH}_2 \\
(1 \text{ atm}) & \\
\end{align*}
\]

- 4.5 x 10^6 g PE (mol of Zr)^{-1} h^{-1}
- Similar to activity observed with MAO/Zirconocene catalysts

\[
\begin{align*}
\text{Zr-Cat.} & \\
\text{Toluene, 23 °C, 0.5 h} & \\
\text{H}_2\text{C}=&\text{CH}_2 \\
(5 \text{ atm}) & \\
\end{align*}
\]

- 2.1 x 10^4 g PE (mol of Zr)^{-1} h^{-1}
- atactic Polypropylene
- NMR control experiment showed that >70% of Zr-cat. undergoes olefin insertion

- Provides direct experimental evidence for abstractive role of group 13 co-catalysts/activators in Ziegler-Natta polymerization

Marks, T. et. al. JACS, 1991, 113, 3623
Mechanism of Ziegler-Natta Polymerization

• Cossee mechanism (1960)

\[
\begin{align*}
\text{Mt} & \quad \text{P} \quad \rightarrow \quad \text{Mt} & \quad \text{P} \quad \rightarrow \quad [\text{Mt} & \quad \text{P}]^+ \quad \rightarrow \quad \text{Mt} & \quad \text{P}
\end{align*}
\]


Key Features:
- Olefin insertion via *cis*-opening of the double bond
- For prochiral olefins, insertion occurs such that non-bonding interactions are minimized (R-groups are trans in the T.S.)

- Can also have a 2,1-insertion (regio-irregular)

• Modified Cossee mechanism (Brookhart-Green-Rooney)

\[
\begin{align*}
\text{Mt} & \quad \text{H} & \quad \text{P} \quad \rightarrow \quad \text{Mt} & \quad \text{H} & \quad \text{P} \quad \rightarrow \quad [\text{Mt} & \quad \text{H} & \quad \text{P}]^+ \quad \rightarrow \quad \text{Mt} & \quad \text{H} & \quad \text{P} \quad \rightarrow \quad \text{Mt} & \quad \text{H} & \quad \text{P}
\end{align*}
\]

agostic: derived from a Greek word, which appears in Homer (trans: to hold or clasp oneself)
Evidence For Agostic Interactions

- Kinetic isotope effects in hydrodimerizations
- Mechanism is similar to Z-N Polymerization

\[
\begin{align*}
\text{Cp}_2\text{ZrCl}_2/\text{MAO} & \quad \overset{\text{H}_2}{\longrightarrow} \\
\text{Cp} & \quad \overset{\text{Zr}^+\text{H}}{\longrightarrow} \quad (\text{Cp}_2)^+ \quad \overset{\text{H}_2}{\longrightarrow} \quad (\text{Cp}_2)^+ \\
\text{Cp}_2\text{ZrCl}_2/\text{MAO} & \quad \overset{\text{H}_2}{\longrightarrow} \\
& \quad \text{Higher oligomers}
\end{align*}
\]

- Hydrodimerizations of deuteriohexene (Brintzinger)

\[
\begin{align*}
\text{Cp}_2\text{ZrCl}_2 (0.1\text{mol}\%) & \quad \overset{\text{H}_2 (15 \text{ atm}), \text{MAO}}{\text{Toluene, } -5 ^\circ\text{C}, 20\text{h}} \quad \overset{\text{anti (threo)}}{\longrightarrow} \quad n-C_4\text{H}_9 \\
& \quad \overset{\text{CH}_2\text{D}}{\text{D}} \quad n-C_4\text{H}_9 + \quad \overset{\text{CH}_2\text{D}}{\text{D}} \quad n-C_4\text{H}_9
\end{align*}
\]

5% yield (anti : syn = 1.3 : 1)

Evidence for Agostic Interactions

- Observed selectivity could be explained by agostic interactions

- Agostic H-interaction lowers T.S. energy relative to agostic-D
Group Exercise

• Further support for agostic interactions from Bercaw

\[
\begin{align*}
\text{H-CH=CH-CH=CH-H} & \quad \xrightarrow{[\text{OpSc(H)(PMe}_3\text{)}] \quad \text{H}_2 \ (\text{4 atm}) \quad 23 \ ^\circ\text{C}} \quad \text{Me-Cyclopentane} \\
\text{D-CH=CH-CH=CH-D} & \quad \xrightarrow{[\text{OpSc(H)(PMe}_3\text{)}] \quad \text{H}_2 \ (\text{4 atm}) \quad 23 \ ^\circ\text{C}} \quad \text{D-Cyclopentane} \\
\text{D-CH=CH-CH=CH-D} & \quad \xrightarrow{[\text{OpSc(H)(PMe}_3\text{)}] \quad \text{H}_2 \ (\text{4 atm}) \quad 23 \ ^\circ\text{C}} \quad \text{D-Cyclohexane}
\end{align*}
\]

GROUP EXERCISE:
1. Provide a mechanism/stereochemical rationale that accounts for the observed KIE in the formation of \textit{d2}-methylcyclopentane.
2. Provide a mechanistic rationale that explains why the selectivity is opposite in the case of \textit{d2}-methylcyclohexane.
Bercaw Solution

1. cis-fused pseudo bicyclic T.S. is favored due to ring strain in the

2. The forming six-membered ring adopts a chair-like conformation in the pseudo bicyclic T.S., which is trans-fused.

Bercaw, J. E., JACS, 1990, 112, 9406
Stereochemical Considerations

- The tacticity and degree of stereo-regularity in PP

$\delta^{13}\text{C}$ is dependent on the configuration of its four stereogenic neighbors

$$[\text{mmmm}] = \frac{\text{int}(\text{mmmm})}{\text{SUM}[\text{int}(\text{pentads})]}$$

$[\text{mmmm}] > 0.95$ is Highly isotactic

Similar eqn applies for syndiotactic

Isotactic $[\text{mmmm}] > 90\%$

Stereochemical Considerations

- Chain-End Control vs. Site Control


- Predicted 13C NMR Patterns

Enantiomorphic Site Control Pentad Distributions

\[
\text{mmm}r : \text{mm}rr : \text{mm}rm : \text{m}rrm = 2 : 2 : 0 : 1
\]
(r-riads)

Chain-End Control Pentad Distributions

\[
\text{mm}mr : \text{mm}rr : \text{mm}rm : \text{m}rrm = 1 : 0 : 1 : 0
\]
(r-dyads)
Isotactic PP from Homogeneous Catalysts

- Ewen studies with racemic and meso ansa-metallocenes

\[
\begin{align*}
\text{Zr-Cat-1:2} & \quad \text{(86 µmol, 56% rac, 44% meso)} \\
\text{MAO 9.4 (mmol)} & \\
\text{Toluene, -60 °C, 4 h} & \\
(2.4 \text{ mol}) & \\
\end{align*}
\]

- 13C-NMR analysis of the triad fragments suggested a mixture of isotactic/atatic-PP

- Author proposed that the isotactic fragment arose from the C2-symmetric cat-2

\[
\begin{align*}
\text{63\% isotactic} & \quad \text{(insoluble in pent.)} \\
\text{37\% atatic} & \quad \text{(soluble in pent.)} \\
\end{align*}
\]

- Later confirmed by Brintzinger using isomerically ansa-metallocene

\[
\begin{align*}
\text{Zr-Cat-3 (3.3 µmol)} & \quad \text{MAO 5.6 (mmol)} \\
\text{Toluene, 23 °C, 0.5 h} & \\
\end{align*}
\]

\[
\begin{align*}
\text{2.7 kg (mol Zr)}^{-1} \text{ h}^{-1} & \quad >95\% \text{ isotactic-PP} \\
\text{Zr-Cat-3} & \\
\end{align*}
\]


Ligand-Controlled PP-Synthesis

• Observations of Ewen and Brintzinger led to further optimization of C₂-Metallocene catalysts

- Highly isotactic-PP can now be achieved with homogeneous C₂ catalysts
- Catalyst productivities and polymer properties are close to modern heterogeneous Z-N catalysts

Productivity: kg of PP/(mmol of M,h).
4th generation heterogeneous Z-N catalyst.


- A question that arose was could syndiotactic polymers also be prepared
Ligand Symmetry and PP-tacticity

- Initial studies by Ewen with $C_S$ metallocenes led to syndiotactic-PP

- Similar ligand optimizations have led to highly syndio-specific catalysts

- PP-tacticity is highly dependent on the ligand symmetry
  $C_S \rightarrow$ Syndiotactic  $C_2 \rightarrow$ isotactic
Unifying Stereochemical Models

\[ \text{C}_2 \rightarrow \text{isotactic} \]

- Polymer chain moves after each insertion (due to metallocyclobutane T.S.)
- Coordination sites are homotopic
- Same prochiral face of the olefin is inserted, regardless of the coordination site

\[ \text{C}_S \rightarrow \text{syndiotactic} \]

- Coordination sites are enantiotopic
- Opposite prochiral faces of the olefin insert at each coordination site

Mechanisms of Racemization

- Site epimerization in $C_S$ catalyst systems ("chain swinging")

\[ \text{Zr-Cat (2 mg)} \rightarrow \text{MAO (2000 eq.)} \rightarrow \text{Toluene/or liq. } C_3H_6, \text{ 0 °C, 0.5 h} \]

Experimental observation:
1. High propene pressure: [rrrr] = 41.8 (moderately syndiotactic)
2. Low propene pressure: [mmmm] = 61.2 (moderately isotactic)

- Author’s proposed that at low [propene] chain swinging is competitive with monomer insertion (enchainment)

Bercaw, J. E. et. al. JACS, 1996, 118, 11988
Mechanisms for Racemization

Mechanisms of Chain Termination

1. Chain transfer to aluminum:

\[ \text{Cp}_2M \text{Me} + \text{Al-Me} \xrightarrow{\text{transfer to Al}} \text{Cp}_2M\text{-Me} + \text{Al-Me} \]

Chain-end epimerization

2. Beta-hydride transfer:

\[ \beta\text{-Hydrogen} \]

\[ \alpha\text{-Hydrogens} \]


Exploiting Site Epimerization

- Catalysts for the synthesis of Hemisotactic-PP

\[
\begin{align*}
\text{Zr-Cat/MAO} & \quad \rightarrow \\
\text{CH}_2=CH_2 & \quad \rightarrow \\
\text{polymer} & 
\end{align*}
\]

- Hemisotactic-PP contain isospecific monomer units separated by monomers of random stereochemistry

- Chiral ligand provides aspecific (random) and isospecific coordination sites

Ewen’s Symmetry Rules

<table>
<thead>
<tr>
<th>Symmetry</th>
<th>Sites</th>
<th>Polymer</th>
</tr>
</thead>
<tbody>
<tr>
<td>$C_{2v}$ Achiral</td>
<td>A, A Homotopic</td>
<td>Atactic</td>
</tr>
<tr>
<td>$C_2$ Chiral</td>
<td>E, E Homotopic</td>
<td>Isotactic</td>
</tr>
<tr>
<td>$C_6$ Achiral</td>
<td>A, A Diastereotopic</td>
<td>Atactic</td>
</tr>
<tr>
<td>$C_6$ Prochiral</td>
<td>E,-E Enantiotopic</td>
<td>Syndiotactic</td>
</tr>
<tr>
<td>$C_1$ Chiral</td>
<td>E, A Diastereotopic</td>
<td>Hemi-isotactic</td>
</tr>
</tbody>
</table>

- Number of well defined ligand are now available for the synthesis of PP-polymers with varying properties.
- Lead to the formulation of Ewen’s symmetry rules.
- What can synthetic chemists do with stereoselective homogeneous polymerization?


*E = enantioselective site; A = nonselective site.*
Kinetic Resolutions of Olefins

- Basic idea

\[
\begin{align*}
\text{Chiral Z-N Catalyst} & \quad \text{k}_S \text{ fast} \\
& \quad \text{k}_R \text{ slow} \\
& \quad \text{(optically active polymer)} \\
& \quad \text{(enriched monomer)} \\
\end{align*}
\]

Where \( k = \text{rate of monomer enchainment} \)

- First experiments were performed by Pino in 1963

\[
\begin{align*}
\text{TiCl}_4, \text{Zn} & \quad (2/1 \text{ ratio Zn/Ti, } \sim 20 \text{ mol\%}) \\
20 \degree \text{C, 236 h} & \quad \text{Polymer} \quad + \quad \text{Optically purity = 2\%} \\
\end{align*}
\]

- Selectivities were very low
- Proof of principle experiment
- Little was known about the catalyst structure

Pino, P. et. al. JACS 1963, 85, 3888.
Kinetic Resolutions with Zr-Metalallocenes

- Homogeneous Zr-catalysts (Bercaw)

1. \(1,3-(CHMe_2)_2C_5H_3\)SiMe_2Cl
2. 2 \(n\)-BuLi
3. SiMe_2Cl_2
4. Zr(NMe_2)_4
5. 2 SiMe_3Cl

- 13C-NMR analysis suggest Isostatic polymers were formed
- Low but significant values of \(s\) were observed for all olefins
- Moderate to good \(s\) for 3,4-dimethyl-1-pentene

- Bercaw, J. E. et. al. JACS, 2004, 126, 8216.
Mechanistic and Stereochemical Rationale

- Authors propose a site epimerization to explain the formation of primarily isotactic polymer.
- Enchainment of the (S)-enantiomer on the right side of the wedge is favored due to steric interactions.
Structure Activity Relationships

- Author’s suggested that increasing steric bulk in the lower right quadrant could lead to higher selectivities

- No further increases in selectivity observed

- Chain-end control could be competing with catalyst

<table>
<thead>
<tr>
<th>olefin</th>
<th>(S)-2 TOF (hr⁻¹)</th>
<th>s = ( \frac{k_S}{k_R} )</th>
<th>(S)-6 TOF (hr⁻¹)</th>
<th>s = ( \frac{k_S}{k_R} )</th>
<th>(S)-7 TOF (hr⁻¹)</th>
<th>s = ( \frac{k_S}{k_R} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me_2SiZrSiMe_2</td>
<td>60 (12)</td>
<td>2.6 (2)</td>
<td>266</td>
<td>2.3 (2)</td>
<td>374</td>
<td>2.5 (1)</td>
</tr>
<tr>
<td></td>
<td>551 (50)</td>
<td>1.8 (2)</td>
<td>299</td>
<td>1.8 (1)</td>
<td>706</td>
<td>1.9 (1)</td>
</tr>
<tr>
<td></td>
<td>46 (10)</td>
<td>2.1 (1)</td>
<td>49</td>
<td>6.4 (7)</td>
<td>111</td>
<td>1.6 (3)</td>
</tr>
<tr>
<td></td>
<td>40 (11)</td>
<td>16.8 (8)</td>
<td>109</td>
<td>12.5 (4)</td>
<td>450</td>
<td>14.0 (2.8)</td>
</tr>
<tr>
<td>Me_2SiZrCl</td>
<td>75 (2)</td>
<td>1.1 (1)</td>
<td>111</td>
<td>1.2 (1)</td>
<td>633</td>
<td>1.2 (1)</td>
</tr>
</tbody>
</table>

Bercaw, J. E. et. al. JACS, 2004, 126, 8216.
Chain-End Control vs. Site Control

- Polymer contains two stereogenic centers
- How can site-control and chain end control be separated
- Authors proposed a co-polymerization with an achiral monomer

Scenario 1: site-control and chain-end control work in concert (s-homopoly > s-copoly)
Scenario 2: site-control and chain-end control oppose each other (s-homopoly < s-copoly)

Bercaw, J. E. et. al. PNAS, 2006, 103, 15303.
Kinetic Resolution of Co-polymerization

\[
\begin{align*}
R\text{CH} = \text{CH}_2 + \text{H}_2\text{C} = \text{CH}_2 \quad & \xrightarrow{(S)-2 \text{ (1-2 mg), MAO (500/1)}} \text{Co-polymer} \\
\text{Toluene/tetradecane, 25 °C} 
\end{align*}
\]

- 13CNMR and mp data were consistent with polymer structures containing few consecutive chiral repeat units.
- Data suggest that for all but one olefin scenario 1 is operative (s-homopoly > s-copoly).
- For 3-methyl-1-pentene site-control and chain-end control work uncooperatively.

- Complex interactions of end-chain and site control make it difficult to rationally design new ligands.

<table>
<thead>
<tr>
<th>Chiral monomer</th>
<th>Entry number</th>
<th>Conv. rate*</th>
<th>Conv. rate*</th>
<th>Conv. rate*</th>
<th>Conv. rate*</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>(s = k_S/k_R)</td>
<td>(k_S/k_R)</td>
<td>(s = k_S/k_R)</td>
<td>(k_S/k_R)</td>
</tr>
<tr>
<td>RCH = CH2</td>
<td>1</td>
<td>2.6 (0.2)</td>
<td>410 (160)</td>
<td>3.4 (0.1)</td>
<td>410 (160)</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>2.6</td>
<td>317 (76)</td>
<td>1.4 (0.1)</td>
<td>317 (76)</td>
</tr>
<tr>
<td>RCH = CH2</td>
<td>3</td>
<td>1.8 (0.2)</td>
<td>190 (6)</td>
<td>1.2 (0.1)</td>
<td>190 (6)</td>
</tr>
<tr>
<td>RCH = CH2</td>
<td>4</td>
<td>2.1 (0.1)</td>
<td>172 (33)†</td>
<td>13 (2)</td>
<td>172 (33)†</td>
</tr>
<tr>
<td>RCH = CH2</td>
<td>5</td>
<td>16.8 (0.8)</td>
<td>143 (8)§</td>
<td>5.1 (0.9)</td>
<td>143 (8)§</td>
</tr>
<tr>
<td>RCH = CH2</td>
<td>6</td>
<td>15.5</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>RCH = CH2</td>
<td>7</td>
<td>7.6 (0.8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Conclusions

(1) Advent of homogeneous catalysts provided a more well-defined system for a mechanistic analysis of Z-N polymerization
(II) Variation of ligand symmetry in the metallocene allowed for the synthesis of a number of different polypropylene structures
(III) Kinetic resolution of olefins using homogeneous catalysts is very promising, but still in its infancy

Karl Ziegler-the last Al-Chemist “...because he turned aluminum into gold.”
Excellent Reviews To Be Aware Of

I. Excellent reviews on stereochemistry and mechanism of Ziegler-Natta Polymerizations:


II. Review on co-catalysts and activators in Ziegler-Natta Polymerization:


III. Reviews on agostic interactions in organometallic complexes:


IV. Chemical Reviews volume 100, issue 4 is dedicated to metal-catalyzed polymerization
Backup: Evidence for MAO-Cluster

Mark R. Mason, Janna M. Smith, Simon G. Bott, and Andrew R. Barron

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