

# Symmetry rules and reaction mechanisms of Ziegler–Natta catalysts<sup>1</sup>

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## Abstract

Symmetry rules obeyed by metallocenes having well-defined, rigid structures are in accord with reaction mechanisms proposed in the 1960s and 1970s for Ziegler–Natta catalysts with unknown structures. © 1998 Elsevier Science B.V.

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## 1. Introduction

Stereospecific polymerizations with chiral metallocenes were first done in 1982 after the possibility was predicted by the RCp steric effects on copolymerization reactivity ratios and the steric effect of a third ligand (the chain-end) caused the formation of isotactic polypropylene with an achiral catalyst (Fig. 1) [1–3].

The main subject of this contribution is chiral metallocene catalyst symmetry effects on polypropylene structures. These polymerization results confirm how Ziegler–Natta catalysts actually work. The catalyst symmetry effects on polypropylene observed in the 1980s and 1990s could have been predicted with theories published in the 1960s and early 1970s.

## 2. Historical

- Long and Shilov suggested polymerization active metallocenes are mono-alkyl cations paired with cocatalyst anions [4–6].
  - Cossee speculated chain growth occurred by a chain migratory insertion mechanism [7].
    - The Cossee–Arlman isotactic-specific propylene polymerization mechanism (Scheme 1) had ‘the growing alkyl group move back to its original position after each incorporation of a new monomer unit’ [8].
      - Allegra concluded that active, heterogeneous polypropylene catalysts have C<sub>2</sub> symmetry because the back-skip reaction in the Cossee–Arlman mechanism has an activation energy of only 5 kcal/mol [9].
        - Zambelli proposed that syndiotactic polypropylene could be made with chiral catalysts [10,11].
          - Zambelli determined that the microstructure of isotactic polypropylene was consistent with stereochemical control by a chiral heterogeneous catalyst [12–14].

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<sup>1</sup> Dedicated to my mentor, Professor Adolfo Zambelli.

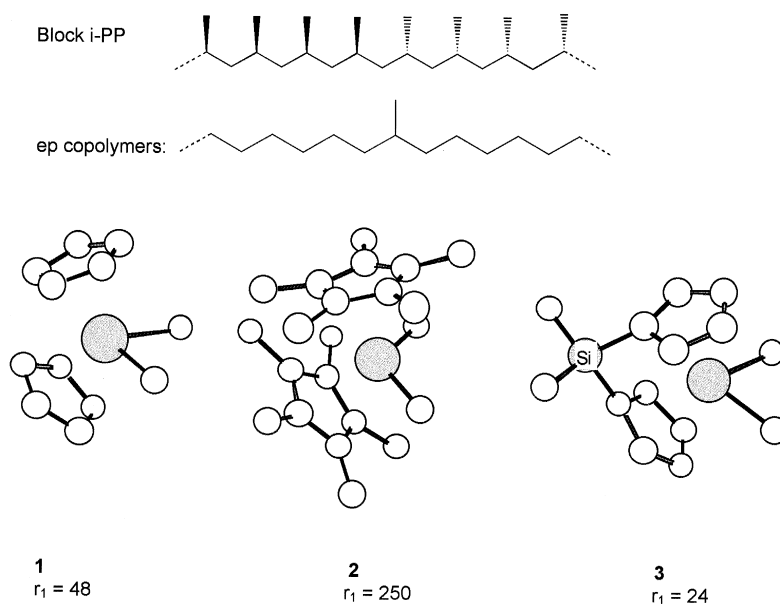
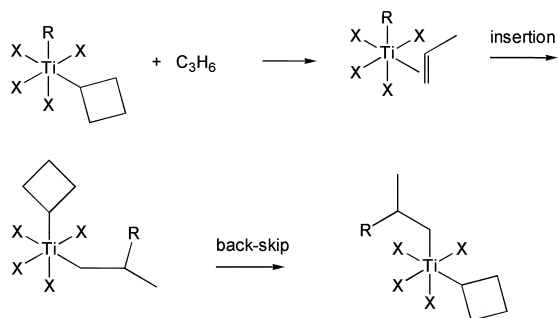


Fig. 1. Microstructure of isotactic polypropylene obtained with  $\text{Cp}_2\text{Ti-R}^+$  and ligand effects in ethylene–propylene copolymerizations with Zr (1).

• Zambelli's isotopic labelling studies [15–18], supported by molecular mechanics calculations of Corradini's group [19], showed that the chain-end is pushed into a specific conformation by the catalyst and acts as a molecular lever; directing which  $\pi$ -face of the monomer bonds to stereospecific catalysts.

### 3. Stereospecific metallocenes

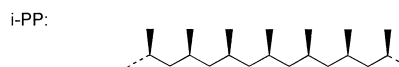
Jordan popularized the now generally accepted theory that the active metallocene cata-



Scheme 1. The Cossee–Arlman mechanism for isotactic polypropylene.

lysts are monoalkyl cations [20]. The symmetry rules discussed in this contribution and the polymer  $^{13}\text{C-NMR}$  'finger-printing' of monoalkyl metallocene cations unambiguously generated from dimethyl metallocene derivatives and  $\text{Ph}_3\text{C}^+$  reagents provided compelling evidence supporting the cation model [21]. The structural defects in the chains are such a sensitive fingerprint that accurately reflects modest differences in the structures of the active sites that it may be concluded that  $\text{MAO}^-$  is a spectator counter-ion playing no significant role in the polymerizations.

Allegra's conclusions made it obvious that a catalyst with  $\text{C}_2$  symmetry was preferable for making isotactic polypropylene (i-PP) with a homogeneous catalyst:



Bridged Cp ligands were clearly required from Zambelli's rationalization on the need for conformational stability of the chain-end [22]

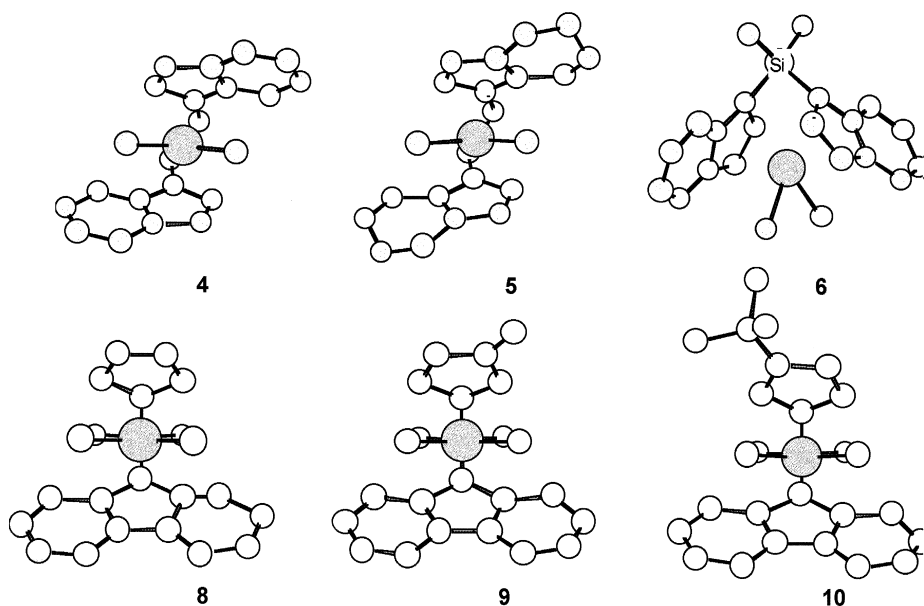


Fig. 2. Models of six bridged, rigid metallocenes that make Isotactic (4, 5, 6, 10), syndiotactic (8), and hemi-isotactic (9) polypropylenes.

and from the bidentate ligand structures used in stereospecific hydrogenations [23]. Potential polymerization catalysts satisfying these two structural requirements were in the open literature since 1979 [24].

The Ti procatalysts **4** and **5** (Fig. 2) fit these requirements and were tested after an unsuccessful first attempt with *rac*-1,3-*n*-Pr[1-Cp-3-*t*-Bu]<sub>2</sub>TiCl<sub>2</sub> [1–3].

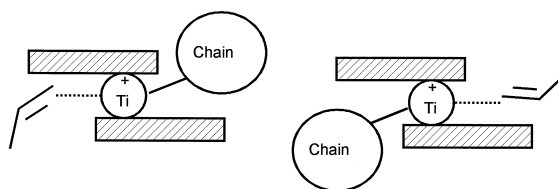
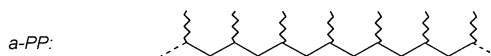
**4** and **5** were the experimental verification of Allegra's theory that C<sub>2</sub> symmetric catalysts make isotactic polymer.

The significantly higher stereospecificity of **5** relative to **4** set the stage for commercially viable isospecific metallocene catalysts to have large substituents β to the bridgehead carbon atoms.

The 2-dimensional drawings in Scheme 2 illustrate why a chain attached to a cationic catalyst derived from **4** and **5** can perform the Cossee–Arlman back-skip reactions in-between monomer insertions with no influence on the polymerization stereochemistry.

Corradini's molecular mechanics calculations are consistent with the chain being pushed by the β-substituent into the indicated orientation and with the monomer experiencing equivalent chiral steric environments; regardless of which side of the catalyst it is bonded to [25–30].

**7**, the *meso*-isomer of **5** with a mirror plane (Fig. 3), predictably produced atactic polypropylene (a-PP) [1–3]:



Scheme 2.

Scheme 3 shows the chain pushed to the more open position. Here there are no forces to put it in any particular direction. In this situation both faces of the propylene have equal access to the catalyst [25–30].

Kaminsky et al. found the Zr analogs of **4** and **5** made waxes at good rates but with melt-

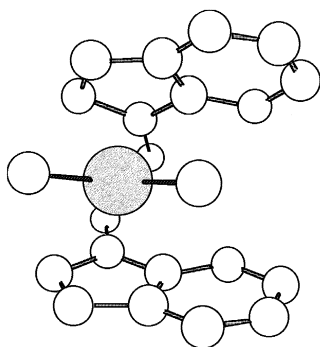


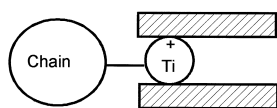
Fig. 3. Molecular model for *meso*-Et[Ind]<sub>2</sub>TiMe<sub>2</sub>.

ing points about 40°C lower and molecular weights 5–10 times less than that of commercial material [31].

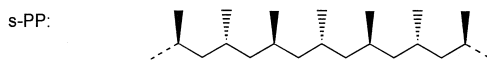
The Hf analogs prepared by Elder and Haspeslagh yielded plastics at fair rates with the proper molecular weights but with melting points that were just as low as those made with Zr [32,33].

Elder made an extremely important contribution to the C<sub>2</sub> symmetric family of metallocenes when he prepared and tested the Me<sub>2</sub>Si bridged **6** [33]. **6** was selected because of the high reactivity of **3** towards propylene (Fig. 1). The higher stereospecificity of **6** over **4** reflects its greater stereorrigidity. This improvement was sufficiently apparent that all of the commercial catalysts later developed by Spaleck and coworkers contained Elder's Me<sub>2</sub>Si bridge [34].

Jones, and then Razavi, prepared **8** with C<sub>s</sub> symmetry [35]. The two non-Cp coordination sites in **8** are mirror images of each other. Scheme 4 illustrates how the propylene monomer experiences steric forces with opposite chiralities on each side of the catalyst; leading to syndiotactic polypropylene (s-PP); as was predicted by Zambelli [15–18].



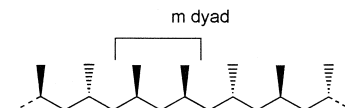
Scheme 3.



Molecular mechanics calculations are consistent with the chain acting as a lever and directing the  $\pi$ -face selectivity [25–30].

The syndiospecificity of **8** was the first definitive experimental evidence that Cossee's chain migratory insertion was operative and provided definitive experimental evidence that the active metallocene catalysts are indeed Long's postulated cationic monoalkyl species in loose association with a cocatalyst anion.

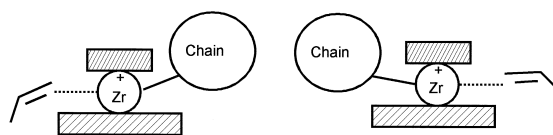
Evidence for the Cossee–Arlman back-skip reaction came when **8**, starved of monomer, proceeded to skip an occasional insertion, creating *meso* (*m*) dyad microstructural defects [36]:



#### 4. Molecular weight control

**8** was the first Zr catalyst to make polypropylene with chain lengths long enough to have a measurable melt index comparable to commercial polymers. The then unusual sensitivity of the molecular weights to propylene concentrations meant that the major termination pathway could not be transfer to monomer [21,37].

Miya et al. had found, at about the same time, that C<sub>2</sub> symmetric catalysts similarly gave higher molecular weights when  $\alpha$ -methyl groups were diagonally across the Cp ring from the  $\beta$ -substituents directing the orientation of the chain-end [38–40]. The diagonal structural similarity between Miya's catalysts and **8** and the



Scheme 4.

differences between them and **6** are illustrated in Fig. 4.

$\alpha,\beta$ -diagonal relationships produce high molecular weight polypropylene because the monomer and polymer are attached to opposite sides of the catalysts. Terminations by  $\beta$ -hydride transfer to monomer are inhibited by a steric contact between the IUPAC carbon C-1 of the monomer and the  $\alpha$ -Cp group if, and only if, the  $\alpha$  group is diagonally across the catalyst from the chain-end. All commercial isotactic and syndiotactic specific Zr catalysts have substituents in this  $\alpha,\beta$ -diagonal relationship. Both the s-PP and i-PP specific systems with the  $\alpha,\beta$ -diagonal substituents have few regio-irregularities from 2-1 insertions for more obvious reasons.

Geometries of the transition state for  $\beta$ -hydrogen transfer to the monomer using the Cerius<sup>2</sup> software package (molecular simulations incorporated) reveal that both the chain-end  $\alpha$ -carbon and C-1 of the monomer are both within 3.0 angstroms of the two fluorenyl carbons  $\alpha$  to the bridgehead carbon in structures **8**, **9**, and **10** (Fig. 5). There is also a contact between the monomer methyl group and a fluorenyl carbon atom  $\beta$  to the bridgehead carbon.

## 5. More recent findings

Jones [21] prepared and tested the C<sub>1</sub> symmetric **9** with our knowledge that a CH<sub>3</sub> group

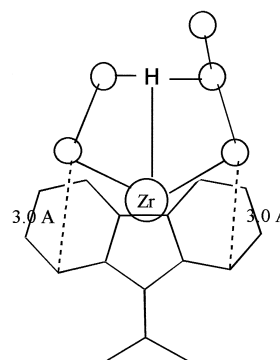
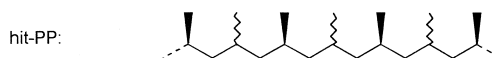


Fig. 5. Illustration of contacts in the transition state for  $\beta$ -hydride transfer from an ethyl group to a propylene monomer with  $\text{Me}_2\text{C}[\text{Cp-9-fluorene}]\text{ZrEt}(\text{propylene})^+$ .

and an aromatic C–H have the same steric requirements from earlier experiments with *rac*-Et[1-Ind-3-Me]<sub>2</sub>ZrCl<sub>2</sub> [33]. The result was a catalyst specific for Farina's elegantly structured hemi-isotactic polypropylene (hit-PP) [41]:



The 2D drawing in Scheme 5 illustrates that once again the chain acts as a molecular lever [25–30].

While the chain is on left side of **9** in the drawing it causes an isotactic insertion. Every other insertion occurs with the chain on the

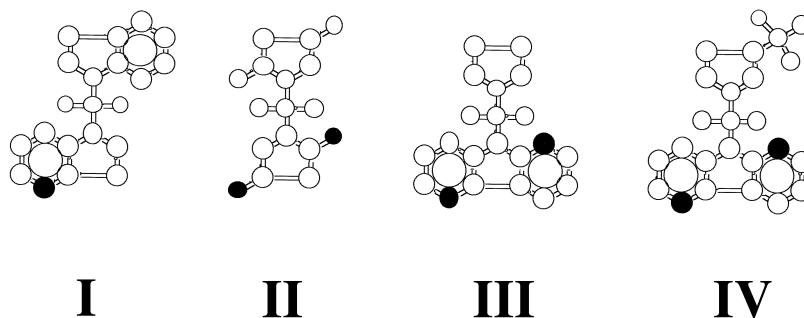
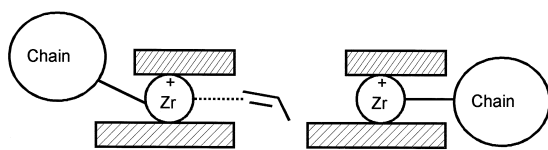


Fig. 4. The  $\alpha,\beta$ -diagonal relationship for Cp substituents needed for high molecular weight, stereoregular polypropylene: (I) low molecular weight isotactic; (II) high molecular weight isotactic; (III) high molecular weight syndiotactic; (IV) high molecular weight isotactic.



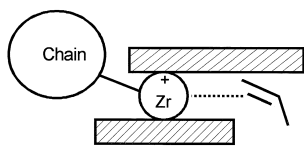
Scheme 5.

crowded side of the catalyst with no forces giving it any preferred orientation. Both faces of the monomer therefore get inserted at equal rates with the chain on the right hand side of **9**. Cossee's and Long's theories are hammered home again.

## 6. Cossee–Arlman

Elder prepared and tested the  $C_1$  symmetric **10** with a  $Me_2Si$  bridge [42,43]. As illustrated in Scheme 6, **10** does isotactic insertions on one side and nothing on the other. Molecular mechanics tells us that the chain is so crowded on the right hand side of **10** that the catalyst pushes the chain back to the less crowded side in a classical Cossee–Arlman back-skip reaction after each monomer is enchainment. The same face of the monomer is repeatedly attached to the more crowded, right hand side.

**10** produced isotactic polypropylene with the same melting point and chain lengths obtained with heterogeneous catalysts. **10** was the first isospecific catalyst with no structural isomers that make atactic polypropylene; a synthetic problem for catalysts with  $C_2$  symmetry. Also, **10** provided the first working model for the Cossee–Arlman mechanism.



Scheme 6.

## 7. Conclusions

Finally, it is noted that the first homogeneous species to produce isotactic polypropylene with high molecular weights and stereoregularities exceeding those provided by conventional heterogeneous catalysts was  $Me_2Si[2-Me-4-Ph-1-indenyl]TiCl_2$  [44–46]. The catalysts need not be Ti. New ligand structures attached to Zr also produce the same kind of highly isotactic polypropylene [42].

Heterogeneous Ti catalysts have at least two chemically distinct types of stereospecific active sites [42,43]. It seems highly likely that both the Cossee–Arlman and the Allegra mechanisms are correct for these heterogeneous catalysts; making both **5** ( $C_2$ -symmetric) and **10** ( $C_1$ -symmetric) valid structural and mechanistic models for them.

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