

Polypropylene Handbook

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Leseprobe

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2.2.2 Trying to Catch up with Ziegler–Natta Catalysts: Isotactic PP

2.2.2.1 Ligand Design for Increasing Molecular Weight

The early isospecific metallocenes produced low molecular weight i-PP: for example, the prototypical Brintzinger's catalyst *rac*-ethylenebisindenylZrCl₂ [28, 29] gives molecular weight of only 20,000 in liquid monomer at 70 °C [30]. This shortcoming, much more than the low isotacticity and melting point, or difficulties of catalyst synthesis, was the major obstacle to the initial development of metallocene catalysts for polypropylene. It was the discovery that a methyl group on the 2-position of indene strongly increases the molecular weight, which opened up the way to the practical use of metallocene PP [31–33]. Beside the necessary substitution on the 2-position, molecular weights are highly dependent on the other substituents, in this case on the size of the substituent on position 4. Very luckily, substitution patterns that increase molecular weights also increase isospecificity. In fact, the combination of substituents on both the 2 and 4 positions of indene in *rac*-Me₂Si(2-Me-4-Ph-Ind)₂ZrCl₂ and related structures, produce PP with both the highest molecular weights and the highest stereoregularity. Molecular weights as high as 1,000,000 can be achieved in liquid monomer at industrial temperatures. On the other hand, addition of a 2-methyl group on 3-alkyl-indenyl ligands is detrimental to molecular weight: *rac*-H₂C(2-Me-3-iPr-Ind)₂ZrCl₂ gives lower molecular weights compared to *rac*-H₂C(3-iPr-Ind)₂ZrCl₂ [26]. In general, C₁-symmetric structures based on fluorene give lower molecular weights than the best C₂-symmetric ones, and are also less active. Some C₁-symmetric structures giving high activities and high molecular weights have been developed, but in the direction of low melting propylene plastomers, which are discussed in Section 2.2.3.

2.2.2.2 Ligand Design for Increasing Isospecificity

As described in Section 2.1, the heterogeneous, donor-modified MgCl₂/TiCl₄ catalysts produce very high molecular weight isotactic polypropylene with molecular weight distributions, which are generally broad. In such PP, apart from very low amounts of amorphous PP, the stereodefects are lumped together in stereoblocks [34]. Therefore, i-PP has a relatively high crystallinity, a T_m of 163–167 °C and a high elastic modulus. In the beginning of metallocene catalyst development, it was found that zirconocenes and hafnocenes are less stereoselective than ZN catalysts. They produce lower melting point and lower molecular weight PP. Twenty years of catalyst development were necessary to produce zirconocene structures, which are even more stereoselective than the ZN catalysts, and produce very high molecular weight PP requiring the use of hydrogen for molecular weight control. Some of the most important structures are shown in Fig. 2.56. However, given the single-center nature of the metallocenes, the few stereochemical or regiochemical errors are randomly distributed in all PP chains, leading to lower melting points (150–160 °C) and lower stiffness compared to ZN PP. This lower crystallinity is not necessarily a shortcoming, as PP with better clarity is obtained, a property useful in applications for which transparency is important, such as in films and injection molded articles (see Section 2.2.6). Brintzinger's zirconocene *rac*-C₂H₄(Ind)₂ZrCl₂ (**1**) and its silyl bridged analogue **2** are among the best studied structures in terms of polymerization performance. Both endowed with high catalytic activity, they produce low melting (T_m 125–

140 °C), low molecular weight iPP, although **2** is slightly better performing than **1**. The 2-methyl-indenyl structure **3**, by providing much higher iPP molecular weights compared to **2**, was the first metallocene to enter the realm of polypropylenes of commercial interest. **4**, with PP molecular weights above 200,000 and **5**, with PP molecular weights above 500,000, a melting point above 150 °C, and a good hydrogen response under practical polymerization conditions, e.g., at 70 °C in liquid propylene, have reached industrial relevance. **5** also has an outstanding activity and is now generally taken as the benchmark for further improvement [35]. Structures **6** [36], **7** [37, 38], and Chisso's **8**, and the many other ones related to them, have been developed to solve specific synthetic, handling, or performance aspects of **5**.

Stereoerrors in PP chains produced with catalyst systems based, for example, on **5** and **6** are at or below the detectability threshold by NMR; the low melting point (T_m 150–155 °C) of PP is due to the presence of regioirregularities (of the 2,1 erythro type). It is worth noting here that in the early systems (such as **1** and **2**), the presence of 2,1 insertions is the cause of lower molecular weights and activities, due to the formation of a slower catalyst state, and to easy β -H transfer after a 2,1 unit (see Scheme 2.1b). On the other hand, the zirconocenes of type **5** and **6**, despite an even lower regioselectivity compared to **1** and **2**, show the highest molecular weights. In fact, the 2-Me-4-Ph substitution pattern increases stereoselectivity partially at the expense of regioselectivity but without increasing chain transfer rates. In this case, a 2,1 unit does not reduce the rate of monomer insertion. This is also proven by the fact that in the presence of small amounts of ethylene, this is found randomly distributed in the polymer chain, and not prevalently after a 2,1 unit.

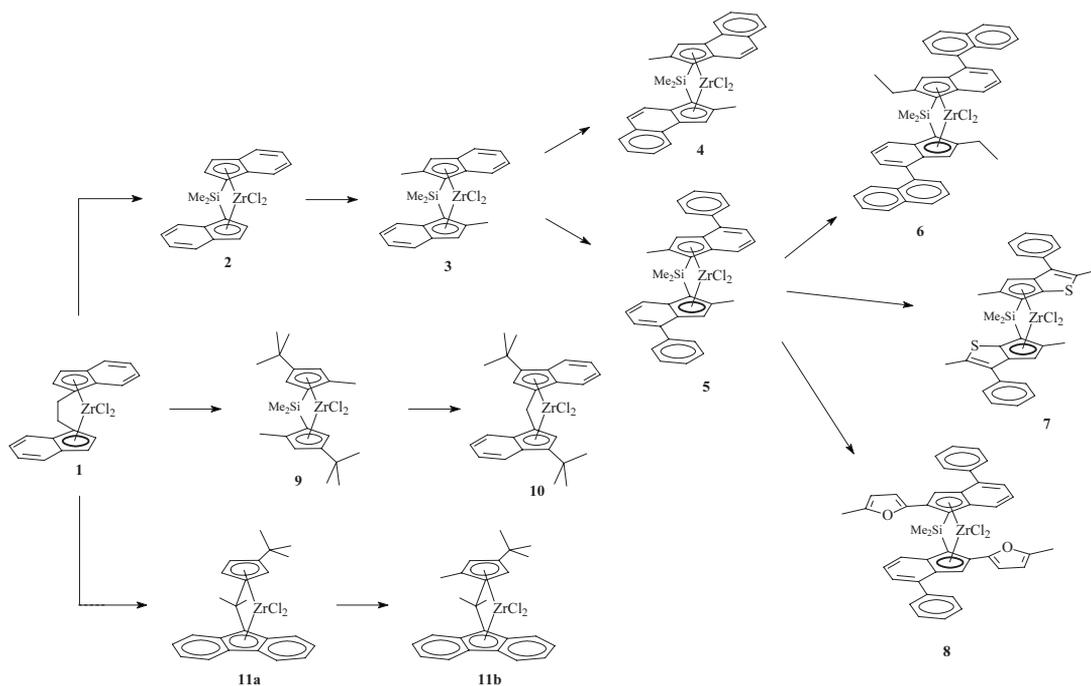


Figure 2.56 Selected C_2 - and C_1 -symmetric isospecific zirconocenes

The zirconocene **9**, bearing 2-Me-*t*-Bu-Cp ligands, is highly isospecific and produces *i*-PP containing low amounts of regioirregularities, but of very low molecular weight [39]. Zirconocene **10**, based on a methylene bridged bis(3-*tert*-butyl-indenyl) ligand, is also among the most stereospecific zirconocenes, and in addition, is fully regioselective producing *i*PP with melting points in the range of 155–160 °C [40]. This structure couples a very easy synthesis with the fact that its meso isomer is inactive. However, **10** produces *i*PP with molecular weights and catalyst activity too low for practical application in PP production. It is clear that, of the different evolutionary branches, the one based on the 2-methyl-4-aryl-indenyl type, developed by Spaleck's team, has been by far the most successful.

2.2.2.3 Influence of Polymerization Conditions

Both polymerization temperature and monomer concentration have an influence on catalyst activity, PP isotacticity, and molecular weight. Regarding the effect of monomer concentration, catalyst activities were found not to obey the classical polymerization rate law

$$R_p = k_p [C^*] [M] \quad (2.12)$$

where C^* is the concentration of activated catalyst species, but show a non-linear dependence on propylene concentration:

$$R_p = k_p' [M]^n \quad (n = 1.4\text{--}1.7) \quad (2.13)$$

This behavior has been rationalized by the coexistence, in the activated metallocene catalyst, of two different active species differing by monomer insertion rates [41]. In this model, the two species are in equilibrium with each other and the position of the equilibrium is determined by the concentration of the monomer, with each active species obeying the rate law of Eq. 2.12. This results in the law expressed by

$$R_p = \frac{k_1 [C^*][M] + k_2 [C^*][M]^2}{k_3 + k_4 [M]} \quad (2.14)$$

The simpler case of a propagation rate of first order in propylene concentration is observed in the case of aspecific metallocenes.

This behavior of the stereoselective metallocenes also affects the laws determining the degree of polymerization as a function of propylene concentration: the general dependence of molecular weight on propylene concentration is given by:

$$\bar{P}_n = \frac{k_1' [M] + k_2' [M]^2}{k_3' + k_4' [M]} \quad (2.15)$$

For the simpler case of a propagation rate first order in propylene concentration, Eq. 2.15 reduces to Eq. 2.16, which can be linearized:

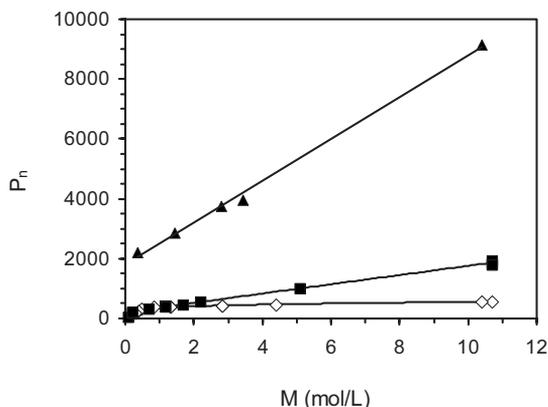


Figure 2.57 Dependence of the average degree of polymerization of isotactic polypropylene on propylene concentration for *rac*-ethylenebisindenylZrCl₂/MAO at 50 °C in toluene (◇), *rac*-Me₂C(3-*t*-BuInd)ZrCl₂/MAO at 50 °C in pentane (■), and *rac*-Me₂Si(2-Me-4-PhInd)ZrCl₂/MAO at 60 °C in hexane (▲). Data from the author's laboratories.

$$\bar{P}_n = \frac{k_p [M]}{k_{t0} + k_{t1} [M]} \Rightarrow \frac{1}{\bar{P}_n} = \frac{k_{t1}}{k_p} + \frac{k_{t0}}{k_p} \frac{1}{[M]} \quad (2.16)$$

As a consequence, the molecular weight of polypropylene increases by increasing propylene concentration. This increase can span more than an order of magnitude (Fig. 2.57). Note that in the three cases shown, the predominant chain release mechanism is different for each catalyst: Brintzinger's catalyst **1** allows both β -H transfer after a 2,1 insertion and after a 1,2 insertion, the fully regioselective catalyst *rac*-Me₂C(3-*t*-BuInd)ZrCl₂/MAO shows mainly β -Me transfer [42], while *rac*-Me₂Si(2-Me-4-PhInd)ZrCl₂, despite being the least regioselective of the three, gives mainly β -H transfer after a 1,2 insertion (even in liquid monomer), with β -Me transfer increasing at the lowest monomer concentrations [43].

This is the basic reason for the limited use of metallocene catalysts in gas phase propylene polymerization processes.

The isospecificity of C₂-symmetric metallocenes in general decreases by decreasing propylene concentration ([propylene]). The same three examples in Fig. 2.57 are shown in Fig. 2.58. Note that *rac*-Me₂Si(2-Me-4-PhInd)ZrCl₂/MAO is more isospecific than *rac*-ethylenebisindenylZrCl₂/MAO and *rac*-Me₂C(3-*t*-BuInd)ZrCl₂/MAO at any monomer concentration ([M]). However, due to the lower regioselectivity of *rac*-Me₂Si(2-Me-4-PhInd)ZrCl₂ compared to *rac*-ethylenebisindenylZrCl₂ (and *rac*-Me₂C(3-*t*-BuInd)ZrCl₂), the net result is that i-PP from *rac*-Me₂Si(2-Me-4-PhInd)ZrCl₂ and Me₂C(3-*t*-BuInd)ZrCl₂ have very similar melting points.

A number of studies have unambiguously shown that in the case of zirconocenes, isotacticity decreases at lower propylene concentrations [44–47], due to unimolecular primary-growing-chain-end epimerization, which scrambles the chirality of the last chirotopic methine of the growing chain. The accepted mechanism of epimerization is shown in Scheme 2.3.

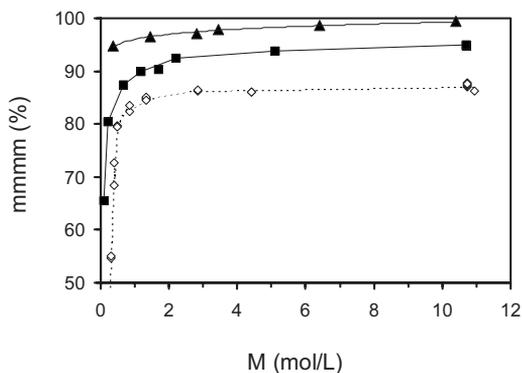
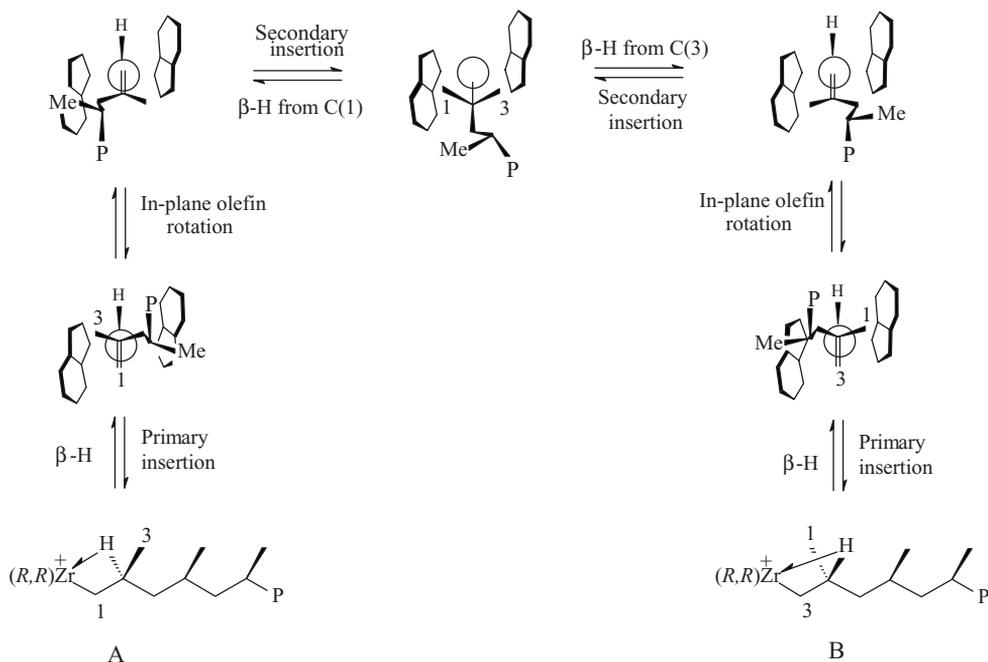


Figure 2.58 Dependence of isotacticity (*mmmm*) on propylene concentration for *rac*-ethylenebis-indenylZrCl₂/MAO at 50 °C in toluene (◇), *rac*-Me₂C(3-*t*-Bulnd)ZrCl₂/MAO at 50 °C in pentane (■), and *rac*-Me₂Si(2-Me-4-PhInd)ZrCl₂/MAO at 60 °C in hexane (▲). Data from the author's laboratories.



The extent of epimerization at a given $[M]$ depends on the polymerization temperature and on the nature of the *ansa*- π -ligand. The dependence of isotacticity on $[M]$ can be described by Eq. 2.17 [17]:

$$\frac{b_{\text{obs}}}{1 - b_{\text{obs}}} = \frac{0.5 + b K_{\text{eq}} [M]}{0.5 + (1 - b) K_{\text{eq}} [M]} \quad (2.17)$$

The Bernoullian probability parameter b is the inherent enantioface selectivity, which depends on the catalyst structure and T_p , but is independent from $[M]$. For most metallocenes, in liquid monomer, $b_{\text{obs}} \rightarrow b$, at least at the polymerization temperature of 50 °C.

Interestingly, these phenomena apply only to C_2 -symmetric metallocenes, while in the case of C_1 -symmetric (and the syndiospecific C_s -symmetric as well) a decrease of monomer concentration either increases the melting point or has no relevant effect. This is due to the mechanism of site epimerization (also referred to as chain back-skip), in which the chain, at the lower monomer concentrations, has a higher chance to migrate to the less hindered site, which is usually also the more stereoselective.

In addition, the influence of temperature is different for different catalyst symmetries. In the case of the C_1 -symmetric systems based on fluorenyl and fluorenyl-like ligand systems, an increase of the polymerization temperature either increases the melting point or has no relevant effect. In the case of the C_2 -symmetric metallocenes, usually higher temperatures cause a decrease of both molecular weights and stereoregularity.

While polymerization temperature and propylene concentration can be varied only within a narrow range in a given polymerization process, hydrogen is commonly used for tuning PP molecular weights, and is particularly effective in the case of zirconocenes.

2.2.3 Beyond Ziegler–Natta Catalysis: Fine-Tuning Stereoregularity

2.2.3.1 Syndiotactic Crystalline and Elastomeric Polypropylene

While on one hand Ziegler–Natta catalysts (ZN catalysts) are by far the most advanced in the production of isotactic polypropylene, on the other hand they are not fully suitable for the production of high-molecular weight polypropylenes of different microstructures. Syndiotactic PP of low stereo- and regioregularity was first reported by Natta and later prepared with vanadium catalysts by Zambelli [13] and Doi [48]. This polymer remained a curiosity, both because of its poor properties and because it had to be prepared at very low temperatures because the mechanism of stereocontrol in this case means a chain-end control (which is most effective at low temperatures) in secondary propagation. The report by Ewen and coworkers, that a metallocene of C_s symmetry was able to produce a highly syndiotactic, fully regioregular polypropylene by site-controlled primary polyinsertion, was thus a clear breakthrough [49]. This finding produced not only a new plastic, but also the proof of the dual-site polymerization mechanism of metallocene catalysts. This mechanism has since been proven by many studies, and has enabled Ewen and others to modify the metallocene ligand framework in order to fully control the microstructure of PP. Figure 2.59 shows the ^{13}C NMR