

CHAPTER III

THEORY

Metallocene compounds are becoming an important class of catalyst for the synthesis of organic molecules and polymers. These complexes also have good potential to act as catalysts or catalyst precursors for a number of organic reactions. The discovery of Group 4 metallocene-aluminoxane systems as catalysts for polymerization reactions has opened up a new frontier in the area of organometallic chemistry and polymer synthesis. Metallocene systems are comprised of 1) bicomponents consisting of a metallocene and an aluminoxane and 2) a single component such as $[\text{Cp}_2\text{MR}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$. The polymerization of monoolefins by metallocenes in comparison to conventional Ziegler-Natta systems offers a versatile possibility to polymer synthesis. The broader flexibility of electronic and steric variations in the cyclopentadienyl (Cp) type ligands allows greater maneuvering in the design of catalyst systems. Such modifications govern the polyinsertion reaction leading to regio- and stereoregular polyolefins.

3.1. Categories of metallocene catalyst systems (Table 3.1) [14]

Homogeneous catalysts consisting of cyclopentadienyls of titanium with aluminum alkyls were found active for ethylene polymerization [15, 49, 50]. These systems were investigated to understand the mechanistic aspects of olefin polymerization, which were difficult to comprehend employing titaniumtetrachloride-based heterogeneous catalysts. A general feature of these homogeneous catalysts is their relatively low activity, viz., 1×10^3 to 4.2×10^3 g.PE.(gTi)⁻¹.h⁻¹.atm⁻¹. However, the addition of small amounts of water was found to increase the activity of these catalyst systems significantly [51].

In the 1980s Sinn, Kaminsky, and coworkers found that metallocenes such as Cp_2ZrCl_2 and Cp_2ZrMe_2 in conjunction with methyl aluminoxane polymerize ethylene with activities in excess of 25×10^6 gPE (gZr)⁻¹ [51]. These catalysts polymerize

propylene to produce atactic polypropylene. In 1985 Kaminsky, Brintzinger, et al. examined the activities of stereorigid metallocenes for propylene polymerization [55]. They found that *rac*-[ethylene(bis-tetrahydroindenyl)]zirconium dichloride in conjunction with methylalumoxane produces isotactic polypropylene. This observation led researchers to examine the potential of a number of stereorigid metallocene compounds for stereospecific polymerization of α -olefins.

Metallocene catalyst systems require a large amount of methylaluminoxane for achieving higher productivity. The high cost of the cocatalyst stimulated the search for new families of metallocenes, which can perform in the absence of aluminoxane. In recent years [56], this has led to the synthesis of a number of cationic metallocenes. Attention is now being paid to incorporate metallocene on inorganic supports such as $MgCl_2$ and SiO_2 to control the fluff morphology of the polymer and prevent reactor fouling [57].

3.1.1. Metallocene

Metallocenes are a class of compounds in which cyclopentadienyl or substituted cyclopentadienyl ligands are π -bonded to the metal atom. Various types of metallocenes have been synthesized and characterized by physicochemical methods [58-62, 63, 64]. The number of known complexes is so large that it restricts the inclusion of synthetic and characterization aspects of metallocenes in this review. Representative examples of each category of metallocenes are shown in Table 3.2. In recent years [65-78], a great deal of attention has been directed at the synthesis of new metallocenes including a variety of cationic types and metallocenes incorporated on inorganic supports such as γ -alumina, $MgCl_2$, and silica [57, 79, 80].

TABLE 3.1
Metallocene Catalyst Systems^a

Catalyst	Cocatalyst	Remark
1. Chlorocyclopentadienyl derivative of titanium: e.g., Cp ₂ TiCl ₂	Dialkylaluminum chloride	Active for ethylene but inactive for propylene polymerization
2. Metallocene catalyst systems containing alumoxane compounds		
2.1 Nonstereorigid metallocenes, e.g., Cp ₂ MX ₂	Alumoxane	a) High activity for ethylene polymerization b) Active for propylene polymerization (atactic polymer)
2.2 Stereorigid metallocenes, e.g., Et(Ind) ₂ MCl ₂	Alumoxane	Active for regio- and stereospecific polymerization of propylene
2.3 Supported metallocene catalysts, e.g., SiO ₂ -Et(Ind) ₂ MCl ₂	Alumoxane/alkylaluminum	Active for ethylene and propylene polymerization
3. Metallocene catalysts systems containing non alumoxane compounds		
3.1 Ionic metallocenes, e.g., [Cp ₂ MR(L)] ⁺ [BPh ₄] ⁻	-	Active for ethylene and propylene polymerization

^aM = Ti, Zr, Hf.

TABLE 3.2
Representative Examples of Metallocenes

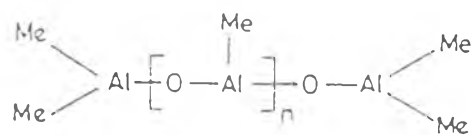
[A] Nonstereorigid metallocenes:	1) Cp_2MCl_2 (M = Ti, Zr, Hf) 2) Cp_2ZrR_2 (R = Me, Ph, CH_2Ph , CH_2SiMe_3) 3) $(\text{Ind})_2\text{ZrMe}_2$
[B] Nonstereorigid ring-substituted metallocenes:	1) $(\text{Me}_5\text{C}_5)_2\text{MCl}_2$ (M = Ti, Zr, Hf) 2) $(\text{Me}_3\text{SiCp})_2\text{ZrCl}_2$
[C] Stereorigid metallocenes:	1) $\text{Et}(\text{Ind})_2\text{ZrCl}_2$ 2) $\text{Et}(\text{Ind})_2\text{ZrMe}_2$ 3) $\text{Et}(\text{IndH}_4)_2\text{ZrCl}_2$
[D] Cationic metallocenes:	1) $\text{Cp}_2\text{MR}(\text{L})^+[\text{BPh}_4]^-$ (M = Ti, Zr) 2) $[\text{Et}(\text{Ind})_2\text{ZrMe}]^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ 3) $[\text{Cp}_2\text{ZrMe}]^+[(\text{C}_2\text{B}_9\text{H}_{11})_2\text{M}]^-$ (M = Co)
[E] Supported metallocenes:	1) $\text{Al}_2\text{O}_3\text{-Et}[\text{IndH}_4]_2\text{ZrCl}_2$ 2) $\text{MgCl}_2\cdot\text{Cp}_2\text{ZrCl}_2$ 3) $\text{SiO}_2\cdot\text{Et}[\text{Ind}]_2\text{ZrCl}_2$

3.1.2. Aluminoxane

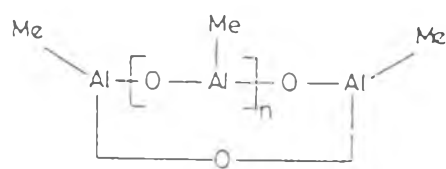
Aluminoxane are synthesized by controlled hydrolysis aluminum alkyls[81-89]. Simple synthetic routes to methylalumoxanes are not available due to the high reactivity of trimethylaluminum with water. Many inorganic hydrated compounds are used as a source of water for preparing aluminoxane from alkylaluminum [90-96]. Hydrating compounds such as $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $\text{Al}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$ are employed. Various physicochemical data, such as compositional analysis, molecular weight determination, mass spectra, x-ray powder diffraction, infrared, and NMR spectroscopy, are used for the characterization of aluminoxanes [52, 54, 97-100]. In spite of these measurements, the structures of the alkyl aluminoxane are not unambiguously known. Methylaluminoxane (MAO) is considered to be the oligomeric (cyclic or linear, Fig.3.1) mixture of $-\text{AlMeO}-$ units [54] containing possibly cluster like or supramolecular aggregates [94, 99, 100]. In metallocene-based catalyst systems, the aluminoxanes appear to have a combination (depending on the nature of the catalyst and the polymerization conditions) of the following functions:

1. Aluminoxane alkylates the metallocene compound and scavenges the impurity [101].
2. Aluminoxane interacts with metallocene generate cationic metallocene alkyl species.

The aluminoxane not only produces the cations but also stabilizes them [102-105]. This view has been gaining support due to isolation of the cationic species [106-113]. Resconi et al. [100] proposed that trimethylaluminum is the actual cocatalyst in $\text{Cp}_2\text{ZrR}_2\text{-MAO-Me}_3\text{Al}$ systems, while MAO acts as a soluble carrier-activator of the ion pair formed upon reaction of the metallocene with trimethylaluminum.



(A) Linear structure



(B) Cyclic structure

Figure 3.1. Plausible structure of methylaluminoxane [14].

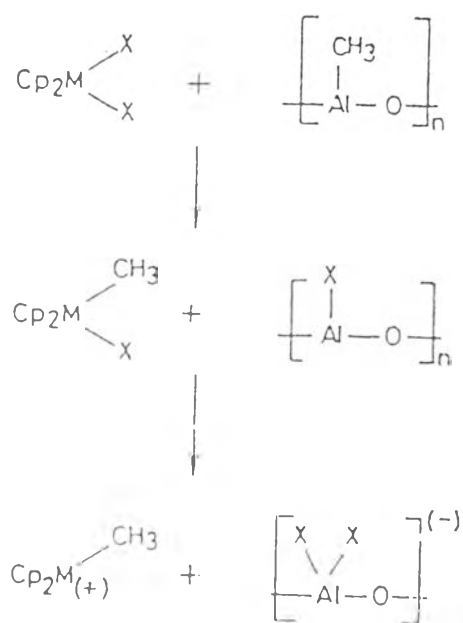


Figure 3.2. Postulated mechanism of formation of the active species in the reaction between metallocenes and methylaluminoxane [119].

3.2. Mechanisms

3.2.1. Interaction of Metallocene with Aluminoxanes and Nature of Active Species

The interaction of metallocene with aluminoxanes has been studied in detail [101, 107, 108, 114-118]. Metallocene dichloride reacts with methyl aluminoxane to yield a methylated compound (Fig.3.2). It undergoes either methyl or chloride abstraction to generate metallocene methyl cations [119, 101, 108]. The research work reported by Marks, Bochmann, Jordan, and others gave synthetic and spectroscopic evidence that cationic metallocenes $[(Cp_2MR)]^+$ are the active species [56, 106, 107, 109-112]. The interaction of dichlorozirconocene, methylchlorozirconocene, and dimethylzirconocene with MAO has been studied by x-ray photoelectron spectroscopy [115]. The results indicate the formation of cationic species is also reported by Marks et al. [107] who studied the reaction of $Cp_2Zr(^{13}CH_3)_2$ with MAO. The solid-state $^{13}CPMAS-NMR$ study at different Al/Zr ratios indicated the formation of a cation like the $Cp_2ZrCH_3^+$ species. The data also indicate that Al:Zr stoichiometry required to form this cation is considerably lower than that employed in a typical catalyst reaction. Siedle et al., [116] employed solution $^{13}C-NMR$ spectroscopy to demonstrate that dimethyl metallocenes such as $Cp_2Zr(^{13}CH_3)_2$, $(Me_5Cp)_2Zr(^{13}CH_3)_2$, $(Indenyl)_2Zr(^{13}CH_3)_2$, $Me_2Si(C_5H_4)_2Zr(^{13}CH_3)_2$, and $Cp_2Hf(^{13}CH_3)_2$ undergo degenerate methyl exchange with methyl acceptor compounds such as Me_6Al_2 and $(MeAlO)_x$ (Reaction 1). The kinetics of degenerate methyl exchange indicate that steric effects are important determinants of the free energy of activation as compared to electronic effects in the formation of cationic species.



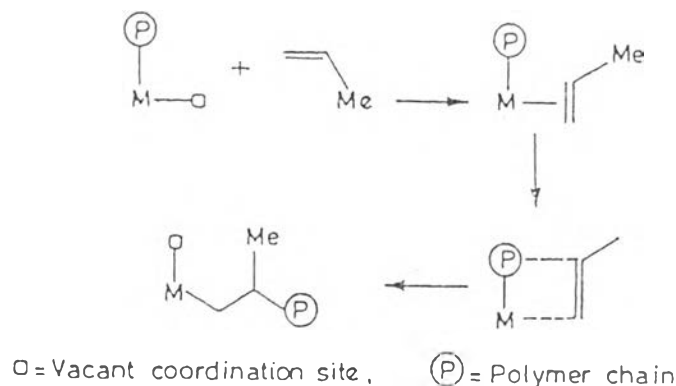


Figure 3.3. Cossee mechanism for Ziegler-Natta olefin polymerization [123].

3.2.2. Mechanism of Polymerization

The mechanism of monoolefin polymerization catalyzed by a highly active metallocene-alumoxane system has been the subject of many experimental and theoretical investigations [120-147]. These studies have shown that the Cossee mechanism of polymerization is indeed viable (Fig.3.3) for metallocene catalysts [125, 148-150]. In the cationic metallocene species, the metal atom is coordinated with the π -ligands and an alkyl group (growing polymer chain). During polymerization, the monomer is coordinated with a highly electrophilic and coordinatively unsaturated cationic complex. It is followed by insertion of a monomer in the metal-carbon bond to produce a polymer chain. The migration of the polymer chain, P, and the formation of the metal-carbon bond occur in concert through a four-center transition state. This results in the recreation of a vacant coordination site at the site originally occupied by the polymer chain. This process involving shifting of the growing chain to the position previously occupied by a coordinated monomer continues until termination of the polymer chain. Modification of the Cossee mechanism of α -agostic hydrogen interaction has also been suggested [137, 138]. Brintzinger et al. provided experimental evidence for such an α -agostic hydrogen interaction in zirconocene-catalyzed polymerization of olefin [139].

Stereoregulation in α -olefin polymerization is one of the most important capabilities of metallocene catalyst systems. Propylene polymerization produces four types of polypropylene: isotactic, syndiotactic, atactic, and hemiisotactic [123, 147] (Fig.3.4). There are two types of stereocontrol mechanism operating: stereochemical control due to chirality of the catalyst (enantiomorphic site control) and stereochemical control due to configuration (chirality) of the last inserted monomer unit (chain end control). These stereocontrol mechanisms do not operate independently in all metallocene catalyst systems. Erker et al. reported [121] that chiral, nonbridged $\text{rac}-(\text{C}_5\text{H}_4\text{CHMePh})_2\text{ZrCl}_2/\text{MAO}$ produces isotactic polypropylene through both chain end control and the enantiomorphic site control mechanism. The polymer obtained (Fig.3.5) consist of 35 % isotactic PP of type 1 (enantiomorphic site control) and 65% of type 2 (chain end control) [121]. A number other of studies [133, 136, 146, 147] have revealed that symmetry of the metallocene mostly affects the tacticity of the polymer. A relationship has also been observed among the stereochemistry of the starting metallocene, the stereocontrol mechanism, and the polymer stereoregularity (Table 3.3).

3.2.2.1. Enantiomorphic-Site Controlled Stereoregulation

The stereorigid ligand environment around the metal is required for the enantiomorphic site-controlled mechanism. It helps in distinguishing the enantiofaces of the prochiral monomer and controlling the orientation of monomer insertion into the M-C bond. Metallocenes such as $\text{rac-Et}(\text{IndH}_4)_2\text{ZrCl}_2$ and $\text{rac-Et}(\text{Ind})_2\text{ZrCl}_2$ with C_2 symmetry yield an isotactic polymer. The configuration of the catalytic complex is ideally the same during isotactic polymerization [123] (Fig.3.6). Defects also occur during the synthesis of isotactic polymer (Fig.3.7). A syndio-type defect takes place when propylene reacts from the opposite prochiral face, whereas secondary defects produce a polymer with two adjacent methine unit. Syndiotactic polymerization [123] of propylene has a regular alternate configuration at adjacent chiral center along the polymer chain (Fig.3.8). A metallocene with C_s symmetry, such as $\text{isopropyl}-(\text{Cp-1-fluorenyl})\text{ZrCl}_2/\text{MAO}$, produces syndiotactic polypropylene. The enantiomorphic site-controlled mechanism has been extended to catalytic complexes yielding hemiisotactic polymer [127, 147]. The mechanism of

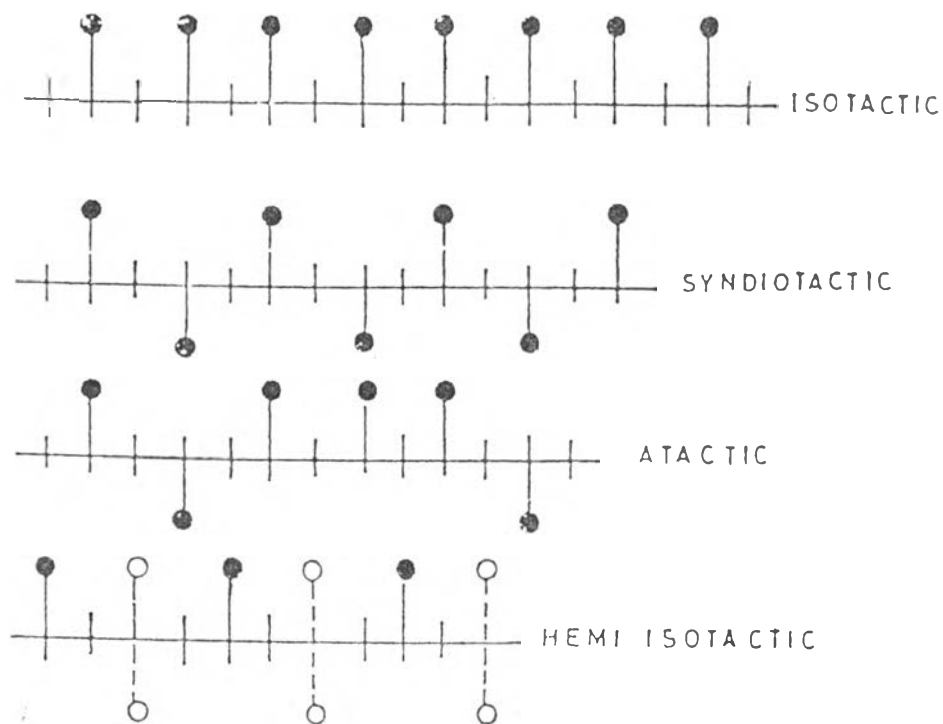


Figure 3.4. Types of olefin polymer tacticity [123] and [147].

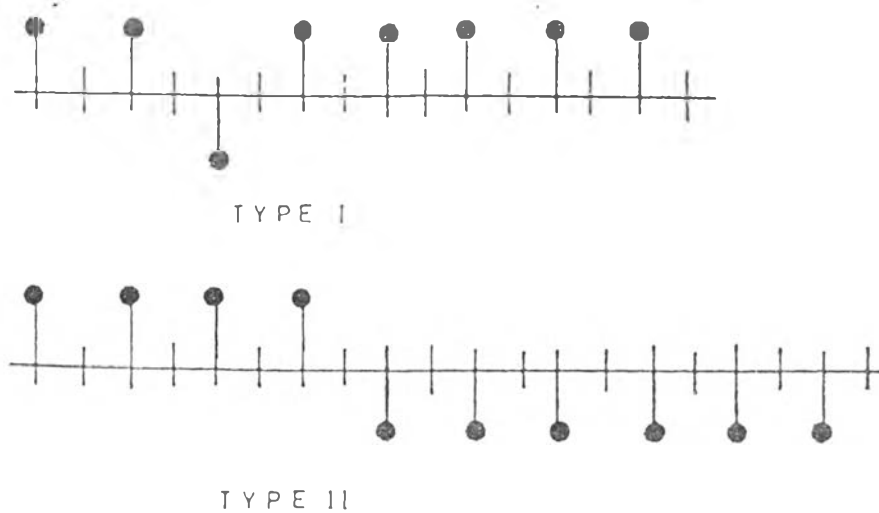


Figure 3.5. Isotactic polypropylene: Type 1, enantiomeric site-controlled mechanism; Type 2, chain-end-controlled mechanism [121].

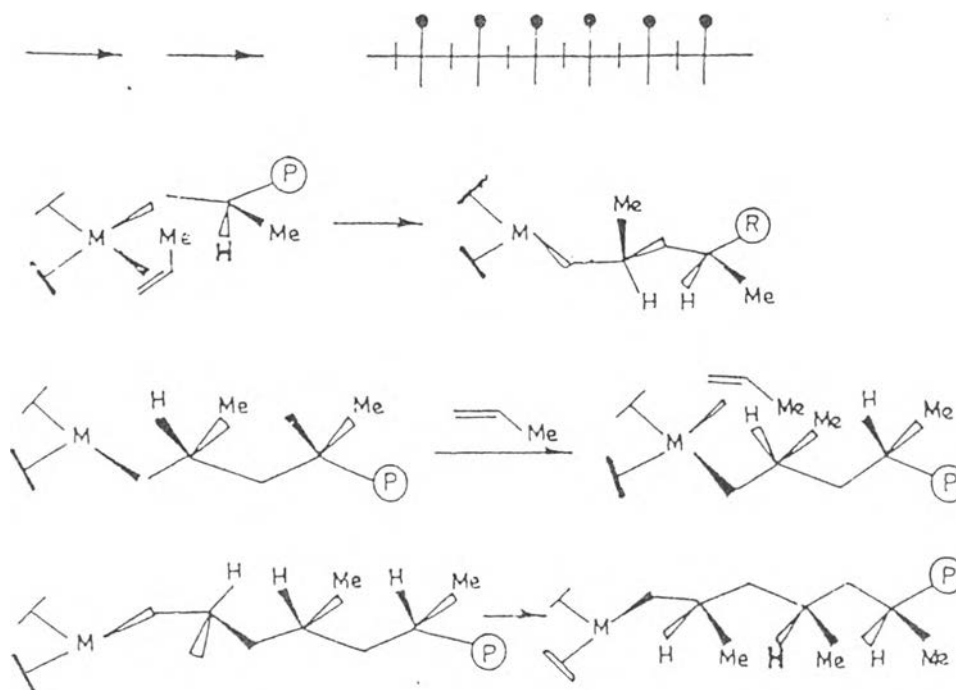


Figure 3.6. Isotactic propylene polymerization by enantiomorphic site-controlled mechanism [123].

polymerization additionally involves an isomerization step either with or without monomer coordination. The metallocene $^1\text{Pr}[3(\text{MeCpFlu})\text{ZrCl}_2/\text{MAO}$ [147] with C_1 symmetry generates hemiisotactic polypropylene.

3.2.2.2. Chain-End Controlled Stereoregulation

In the case of achiral metallocene, the selection between the two faces of the prochiral monomer is dictated predominantly by the configuration of the asymmetric center of the last inserted monomer unit [144]. The catalyst system $\text{Cp}_2\text{TiPh}_2/\text{MAO}$ produces isotactic polypropylene by a chain-end controlled mechanism (Fig.3.9) [120]. The isotactic polypropylene produced by a chain-end stereocontrol involves an occasional change in the configuration of the last inserted monomer unit with tends to be perpetuated (Fig.3.5). The $\text{Cp}_2^*\text{MCl}_2/\text{MAO}$ catalyst system polymerizes 1-butene to a predominantly syndiotactic poly(1-butene) [126]. This is the first example of the syndiospecific chain-end control (Fig.3.9) mechanism for a metallocene catalyst system.

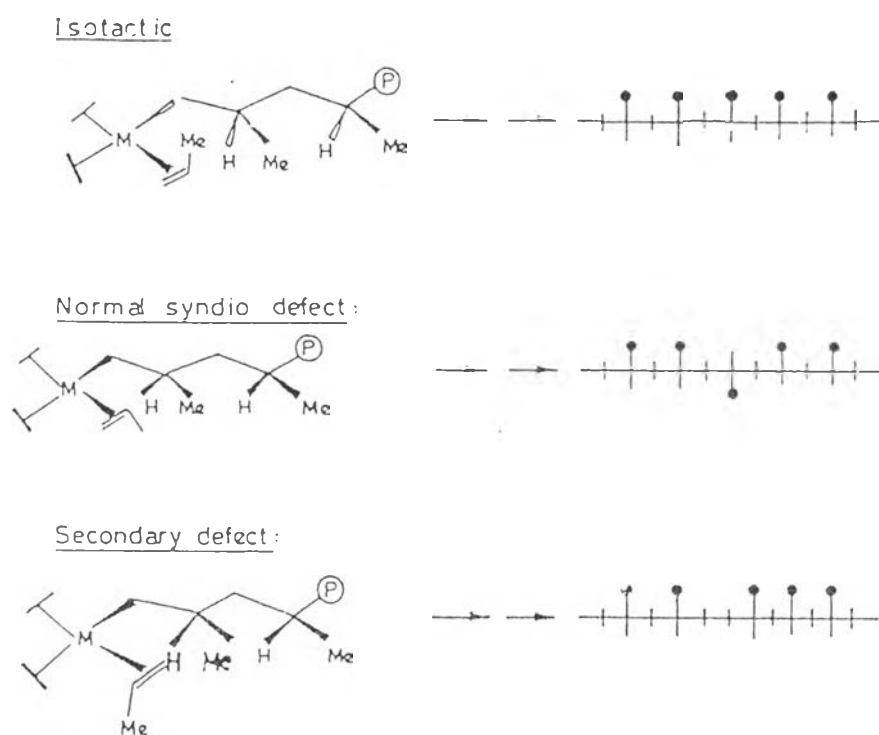


Figure 3.7. Stereodefects in an isotactic polymer chain [123].

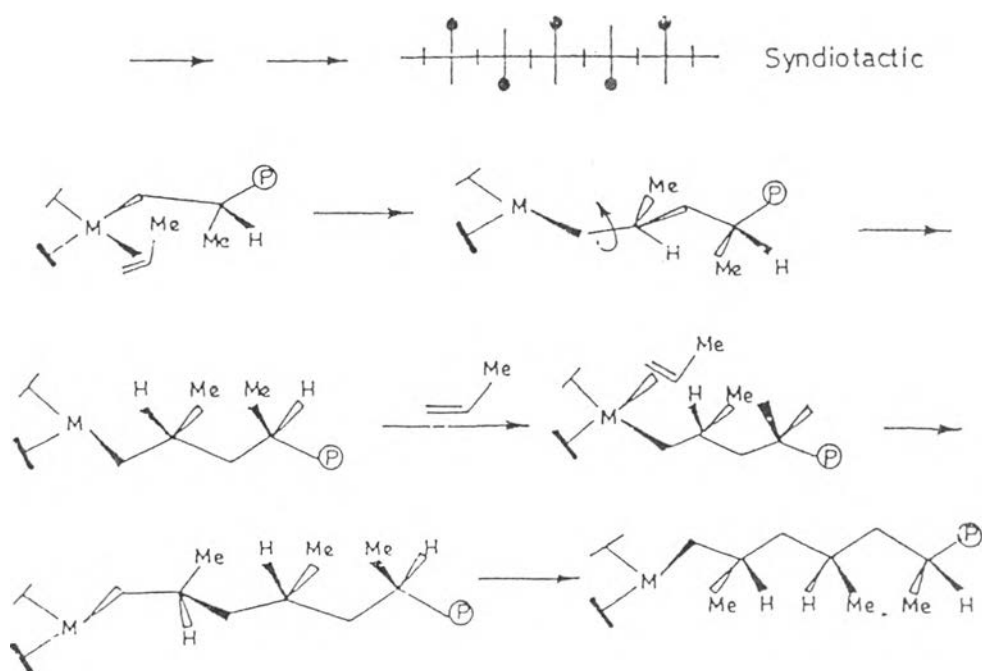


Figure 3.8. Stereoregulation for syndiotactic propylene polymerization by enantiomorphic site-controlled mechanism [123].

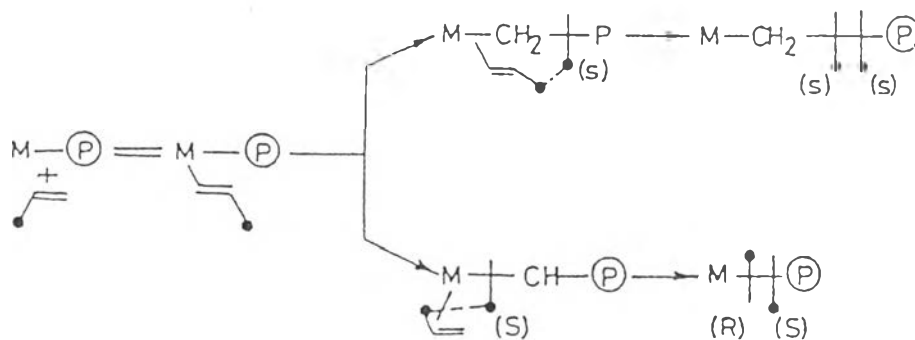


Figure 3.9. Stereochemical chain-end-controlled syndio- and isotactic propylene polymerization [120].

3.2.3. Chain Transfer Mechanism

In metallocene-catalyzed olefin polymerization, the termination of polymer chain [151, 152] occurs through a chain transfer involving β -H elimination (Fig.3.10) [153] and β -Me elimination (Fig.3.11) [154, 155]. The termination of a polymer chain may also occur due to chain transfer to aluminum (Fig.3.12) [100, 156], monomer (Fig.3.13) [157, 158], or hydrogen (Fig.3.14) [158]. All of the mechanisms proposed above are dependent on the nature of the metallocene, alumoxane, and the polymerization conditions. Resconi et al. [151] studied the contribution of various chain transfer processes in the propylene polymerization reaction due to the different metallocenes and reaction conditions (Table 3.4). $\text{Cp}_2^*\text{MCl}_2/\text{MAO}$ (Cp_2^* = pentamethylcyclopentadienyl; $\text{M} = \text{Zr}, \text{Hf}$) gives atactic propylene oligomers and low molecular weight polymers. The GC-MS and ^1H and ^{13}C NMR analyses of the products show the presence of unsaturated and saturated end groups. The unsaturated end groups contain vinylidene and allyl groups. Product analysis shows the both M-CH_3 and M-H bonded active species are involved in the chain termination step involving β - CH_3 or β -H elimination.

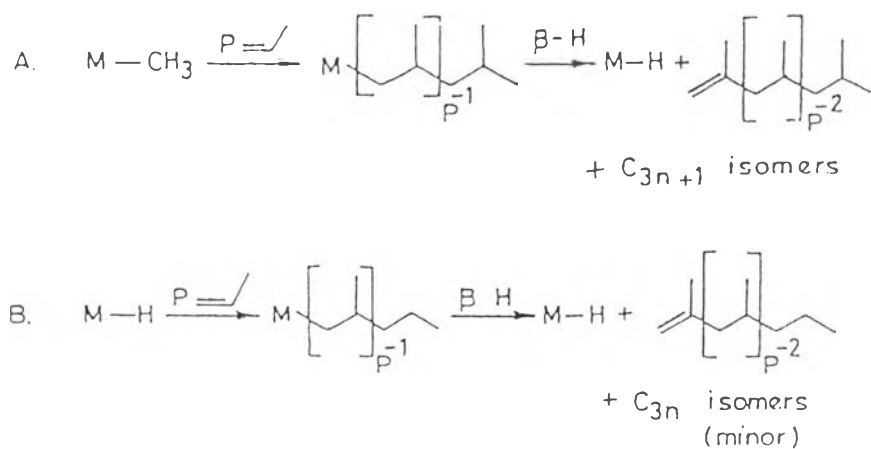


Figure 3.10. Chain transfer via β -H elimination [151].

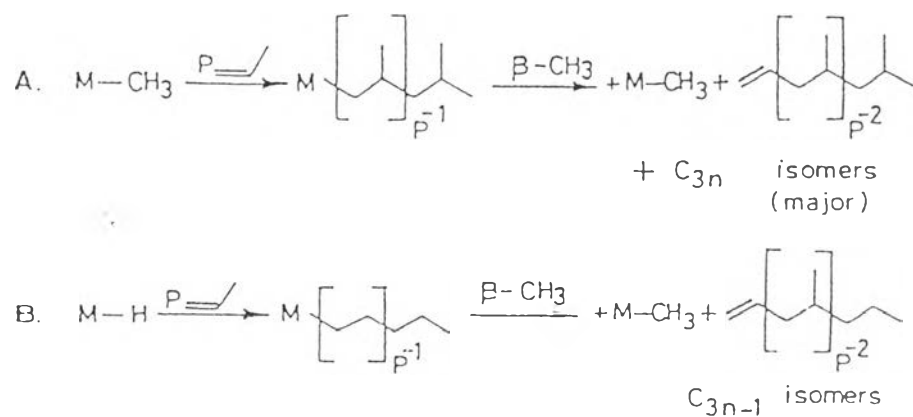


Figure 3.11. Chain transfer via β -Me elimination [151].

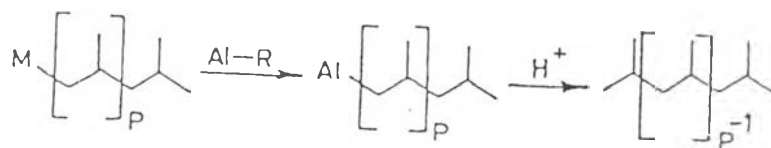


Figure 3.12. Chain transfer to aluminum [151].

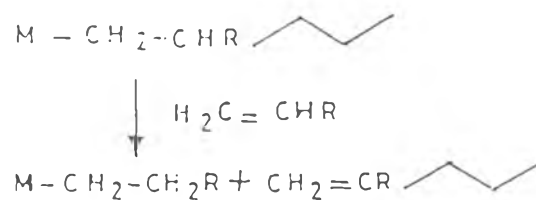


Figure 3.13. Chain transfer to monomer.

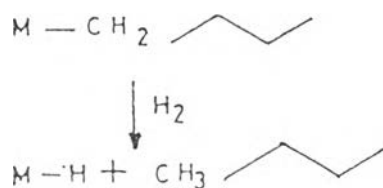


Figure 3.14. Chain transfer to hydrogen.

TABLE 3.3
Relationship between Stereochemistry of the Metallocene and Polymer Microstructure

Metallocene system	Symmetry of metallocene	Polymer	Microstructure	Stereocontrol mechanism	Ref.
rac-Et(IndH ₄)ZrCl ₂ /MAO	C ₂	Polypropylene	Isotactic	Enantiomorphic site controlled	123
Meso-Et(IndH ₄)ZrCl ₂ /MAO	C _s	Polypropylene	Atactic	Enantiomorphic site controlled	123
Isopropyl(Cp-1-flu)ZrCl ₂	C _s	Polypropylene	Syndiotactic	Enantiomorphic site controlled	123
Isopropyl(3-MeCp-flu)ZrCl ₂ /MAO	C ₁	Polypropylene	Hemi-isotactic	Enantiomorphic site controlled	127
Cp ₂ TiCl ₂ /MAO	C _{2v} achiral	Polypropylene	Atactic	Chain end controlled	
Cp ₂ TiPh ₂ /MAO	C _{2v} achiral	Polypropylene	Isotactic	Chain end controlled	120
Cp ₂ *MCl ₂ /MAO	C _{2v} achiral	Poly(1-butene)	Syndiotactic	Chain end controlled	126
rac(C ₅ H ₄ CHMePh) ₂ ZrCl ₂ /MAO	C ₂ achiral	Polypropylene	Isotactic	Chain end and enantiomorphic controlled	121

TABLE 3.4
Percentage of Chain Transfer Mechanisms in Polypropylene Samples^a [151]

Metallocene	T _p (°C)	B-H	B-Me	Al-tr
Cp ₂ ZrCl ₂	50	100	-	-
Cp ₂ ZrCl ₂	0	100	-	-
Cp ₂ HfCl ₂	50	100	-	-
Cp ₂ [*] ZrCl ₂	50	7.9	91.1	1
Cp ₂ [*] ZrCl ₂	0	7.1	81.8	11.1
Cp ₂ [*] ZrCl ₂	-40	-	-	100
Cp ₂ [*] HfCl ₂	50	2	98	Traces
Cp ₂ [*] HfCl ₂	0	2.0	62.7	35.3

^aCp = cyclopentadienyl; Cp^{*} = pentamethylcyclopenta- dienyl. Percentages calculated from the relative intensities of different end groups; B-H = vinylidene; B-Me = allyl; Al-tr = (isobutyl alkyl)/2.

3.3. Metallocenes and Structural Symmetry

Since the humble beginnings of the field [159-162], several varieties of metallocene types and compositions have emerged. When the two π -carbocyclic ligands on either side of the transition metal are unbridged, the metallocene is nonstereorigid and it is characterized by a C_{2v} symmetry. When the ligands are bridged, the stereorigid metallocene, called ansa metallocene, could be characterized by either a C_1 , C_2 , or C_s symmetry as schematically illustrated [163] in Figure 3.15. Note that the two π -carbocyclic ligands on either side of the transition metal for the C_s -symmetric metallocenes need not be identical.

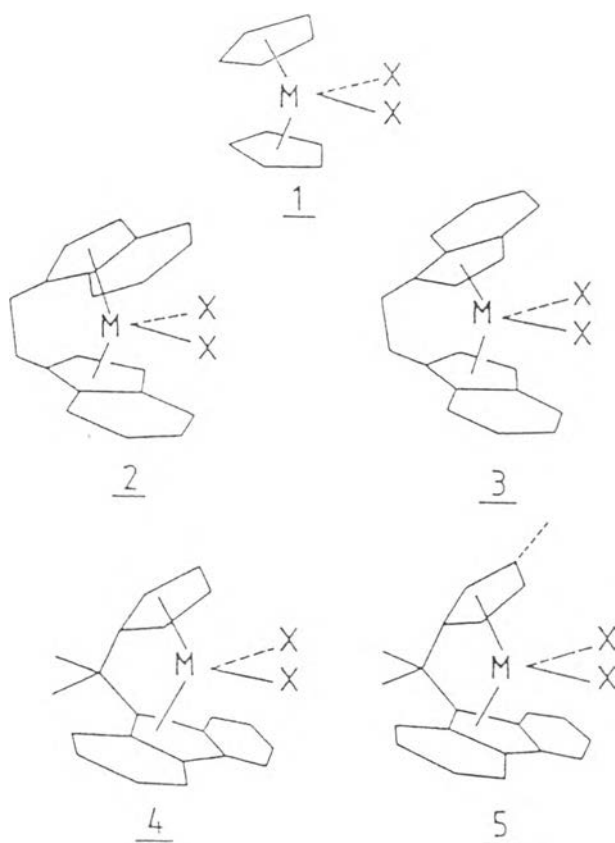


Figure 3.15. Schematic representation of metallocene symmetry. Type 1 is C_{2v} -symmetric; Type 2 is C_2 -symmetric; Type 3 is C_s -symmetric; Type 4 is C_s -Symmetric; Type 5 is C_1 -symmetric [163].

Atactic polypropylene and poly(α -olefin)s normally result from the use of achiral C_{2v} -symmetric metallocenes; hemi-isotactic polypropylene (where every other methyl group has an isotactic placement, the remaining methyls being randomly placed) and poly(α -olefin)s normally result [164] from the use of C_1 -symmetric metallocenes; isotactic polypropylene and poly(α -olefin)s normally result from the use of chiral C_2 -symmetric metallocenes; and syndiospecific propylene and α -olefin polymerizations normally result from the use of C_s -symmetric metallocenes [165]. There are exceptions to this apparent generalization occasioned by the fact that stereospecificity is due to the combined effects of the metallocene symmetry, the chirality of the catalytically active center, and the configuration/chirality of the last-inserted monomer unit.

For example, C_s -symmetric metallocenes could be isospecific, depending on the position, number, and type of substituents on the π -carbocyclic ligands as well as the transition metal type. The meso form of the stereorigid titanocene [164,166], namely, meso-En(4,5,6,7-IndH₄)₂TiCl₂, is achiral and nonstereospecific even though it is stereorigid; it yields atactic polypropylene and poly(α -olefin)s. On the other hand, the analogous rac-En(4,5,6,7-IndH₄)₂ZrCl₂ is chiral and stereospecific; it catalyzes the isotactic polymerization of propylene or α -olefins [164, 167, 168]. Partially isotactic polypropylene has been produced [169] with the use of achiral nonstereorigid Cp₂TiPh₂ at low temperatures. A nonexhaustive list of the C_{2v} -, C_2 -, and C_s -symmetric metallocenes is presented in Tables 5, 6, and 7, respectively. Two examples of C_1 -symmetric metallocenes [164, 170] are as follows: i-Pr[(3-MeCp)(flu)]ZrCl₂ and Me₂C(3-MeCp)(Flu)ZrCl₂.

The detailed polymerization mechanisms of metallocene-aluminoxane catalyst system could still benefit from some new insights. However, there is a general consensus that the active site of the metallocene/MAO system is generated via the alkylation of the metallocene [171, 172] and subsequent abstraction of a methyl group by the alminoxane as depicted in Fig.3.16. The active species is believed to be a 14-

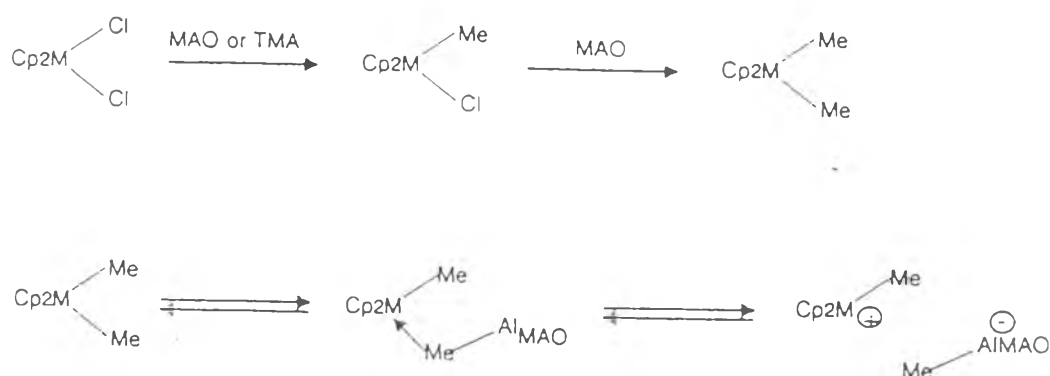


Figure 3.16. Generation of the cationic alkylmetallocenium active site [171].

valence electron cationic alkylmetallocenium ion; the adjunct $[\text{MAOR}]^-$ anion is essentially noncoordinating. The incoming monomer $[\text{H}_2\text{C} = \text{CHR}]$ coordinates with the cationic alkylmetallocenium ion $[\text{Cp}_2\text{MR}]^+$, and is inserted, via the metal-carbon bond $[\text{Cp}_2\text{MR}-\text{H}_2\text{C}-\text{CHR}]^+$, into the previous monomer as the growing chain migrates through the four-center transitional state, regenerating the vacant coordination site for the next incoming monomer [173-177].

Each successive monomer unit is similarly added to the growing polymer chain $[\text{Cp}_2\text{MR}-\text{H}_2\text{C}-\text{CHR}-\text{polymer chain}]^+$. Stereospecific polymerization could arise either from the chiral β -carbon atom at the terminal monomer unit of the growing chain (i.e., chain end control) or from the catalyst site (i.e., enantiomorphic site control) [170, 178]. Steric hindrance of the ligands surrounding the active center plays a role in its stereoselectivity and its stability could be considerably enhanced in several ways. A benzoannulation means of stabilization has been demonstrated [179] for the C_2 -symmetric $\text{Me}_2\text{Si}(\text{BenzInd})_2\text{ZrCl}_2$.

Depending on the metallocene catalyst, the cocatalyst, and the reaction condition, the growing polymer chain could terminate either by (a) a β -hydride elimination [180, 181] or (b) a β -methyl elimination [182, 183] or (c) a chain transfer to the cocatalyst, monomer, or hydrogen [167-168,184] or (d) a combination of the above three [181].

Unlike the conventional heterogeneous Ziegler-Natta catalyst system, the metallocene catalyst system has the advantage of producing polyethylenes having terminal unsaturation which could be used for building functionalities in the polymer. Also, hydrogen could be used for controlling the molecular weight and the corresponding polydispersity index of the metallocene-base polyolefins [167-168, 185]. A judicious use of hydrogen is necessary, however, as its presence could induce the hydrogenolysis of metalloceniumcarbon bonds rather than β -hydride elimination as demonstrated with the $\text{En}(\text{H}_4\text{Ind})_2\text{ZrMe}_2/\text{MAO}$ system in propylene polymerization [186, 187].

Other important independent variables that affect metallocene reactivity and its stereospecificity are the catalyst preactivation, cocatalyst type and composition, comonomer type and composition, and reaction temperature. The polyolefins' molecular weight characteristics are not only catalyst-dependent, they also depend on the mechanism of stereocontrol. Because the metallocenes' structures are unperturbed in solution, solution polymerization facilitates the study of the relationship between the metallocene symmetry and the resulting polyolefin properties. In what follows, the discussion will be conveniently delineated according to the metallocene symmetry.

TABLE 3.5
Selected List of C_{2v} -Symmetric Metallocenes

Metallocenes	Ref.
Zirconocenes (with indenyl ligands)	
Ind ₂ ZrCl ₂	260, 209, 229
Ind ₂ ZrMe ₂	239, 217, 177
Ind ₂ ZrBz ₂	221
(5,6-H ₂ Ind) ₂ ZrCl ₂	221, 222
(5,6-MeInd) ₂ ZrCl ₂	221, 222
(5,6-OMeInd) ₂ ZrCl ₂	221, 222
(5,6-Cl ₂ Ind) ₂ ZrCl ₂	221, 222
Zirconocenes (with cyclopentadienyl ligands)	
Cp ₂ ZrCl ₂	217,260,162,167,239,177,218, 208-210,259,218,229,258,262
CpZrCl ₃	167
Cp ₂ ZrMeCl	260, 263-265, 259
Cp ₂ ZrMe(THF [*])	266
Cp ₂ ZrMe ₂	239,217,209,263-265,259,229
Cp ₂ ZrPh ₂	239, 217, 177
Cp ₂ Zr(CH ₂ C ₆ H ₅) ₂	239, 217, 177
Cp ₂ Zr[CH ₂ SiMe ₂] ₂	239, 217, 177
Cp ₂ Zr(NEt ₂) ₂	256
(n-MeCp) ₂ ZrCl ₂	219
(Me ₅ Cp) ₂ ZrCl ₂	259, 237, 238
Cp(Me ₅ Cp)ZrCl ₂	259
(Me ₅ Cp) ₂ ZrMe ₂	237, 238, 252, 253
(SiMe ₃ Cp) ₂ ZrCl ₂	267, 268
Me ₂ Si(Cp) ₂ ZrCl ₂	200, 204, 205
(n-BuCp) ₂ ZrCl ₂	237, 238
Cp ₂ ZrHex ₂	239
(Cp [*]) ₃ ZrMe ₂	246
(Cp [*]) ₂ ZrMe ₂	246
Titanocenes (with cyclopentadienyl ligands)	
(MeCp)TiCl ₃	204, 247, 255
Cp [*] TiCl ₃	269-273
CpTiCl ₃	269-273
RCpTiCl ₃	255
Cp ₂ TiCl ₂	172, 191
Cp ₂ TiMe ₂	274
Cp ₂ TiPh ₂	239, 166, 184, 228, 229
Cp ₂ TiEnCl	162, 231-232
Hafnocene (with cyclopentadienyl ligands)	
Cp ₂ HfCl ₂	191, 209, 229
Cp ₂ HfMe ₂	239
Cp ₂ HfPh ₂	239

TABLE 3.6
Selected List of C₂-Symmetric Metallocenes

Metallocenes	Pentad (%)	Ref.
Zirconocenes (with indenyl ligands)	m m m m	
En(Ind) ₂ ZrCl ₂	%	236,165,191,193,198,208,209,218
En(4,5,6,7-IndH ₄) ₂ ZrCl ₂	57-93	217,236,165,178,191,198-200
En(5,6-H ₂ Ind) ₂ ZrCl ₂	89.8-98	221, 222
En(5,6-Me ₂ Ind) ₂ ZrCl ₂	na	221,222
En(5,6-OMe ₂ Ind) ₂ ZrCl ₂	na	221, 222
En(4,5,7-IndH ₄) ₂ ZrMe ₂	na	167, 168
En(3-Me ₃ SiInd) ₂ ZrCl ₂	na	191,193,227,240,241
Me ₂ Si(Ind) ₂ ZrCl ₂	na	236,179,202,208-210,218,225,240
Me ₂ Si(4,6-iPr-Ind) ₂ ZrCl ₂	82.2-95	202
Me ₂ Si(4,5,6,7-IndH ₄) ₂ ZrCl ₂	80-90	236,202,208-210,218,225,240,241
Me ₂ Si(BenzInd) ₂ ZrCl ₂	84.5-85	179, 205
Me ₂ Si(4,5-BenzInd) ₂ ZrCl ₂	88-90	202
Me ₂ Si(2Me-4,5-BenzInd) ₂ ZrCl ₂	88-90	275
Me ₂ Si(2-MeBenzInd) ₂ ZrCl ₂	88.7	179, 188, 205
Me ₂ Si(2-MeInd) ₂ ZrCl ₂	92,93	179, 188, 205, 275
Me ₂ Si(2-Me-4iPr-Ind) ₂ ZrCl ₂	88.5-90	275
Me ₂ Si(2Me-4Ph-Ind) ₂ ZrCl ₂	88.6	275
Me ₂ Si(2Me-4Naph-Ind) ₂ ZrCl ₂	95.2	275
Me ₂ Ge(2Me-4Ph-Ind) ₂ ZrCl ₂	99.1	275
MePhSi(Ind) ₂ ZrCl ₂	na	193, 227, 240, 241
i-Pr(Ind) ₂ ZrCl ₂	na	193, 227, 240, 241
Ph ₂ Si(Ind) ₂ ZrCl ₂	na	236,165,193,208-209,227,240,241
Bz ₂ Si(Ind) ₂ ZrCl ₂	na	165
(1,4-butanediyl)silylene(Ind) ₂ ZrCl ₂	na	274
	na	
Zirconocenes (with cyclopentadienyl ligands)		
En(Cp) ₂ ZrMe ₂	na	209, 219
Et ₂ Si(3-MeCp) ₂ ZrCl ₂	90	165, 198-200
Me ₂ C-CMe ₂ (2-H-4-t-BuCp) ₂ ZrCl ₂	62	205
Me ₂ Si(2-Me-4-t-Bu-Cp) ₂ ZrCl ₂	94-96	179,188,200,202,204,205,275
Me ₂ Si(2-Me-4-i-Pr-Cp) ₂ ZrCl ₂	73	179, 188, 200, 204, 205
Me ₂ Si(2-H-4-t-BuCp) ₂ ZrCl ₂	77	179, 188, 200, 204, 205
Me ₂ Si(2,H-4-i-Pr-Cp) ₂ ZrCl ₂	na	179, 188, 200, 204, 205
Me ₂ Si(2,4-Me ₂ -Cp) ₂ ZrCl ₂	89.2	275
Me ₂ Si(4-t-Bu-Cp) ₂ ZrCl ₂	na	200, 204, 205
Me ₂ Si(4-i-Pr-Cp) ₂ ZrCl ₂	na	200, 204, 205
Zirconocenes (with fluorenyl ligands)	31.2-	
PhEn(1,2-Flu) ₂ ZrCl ₂	64.1	195
Hafnocenes (with indenyl ligands)		
En(Ind) ₂ HfCl ₂	68-94	236,165,198-200,206-209,229,242
Me ₂ Si(Ind) ₂ HfCl ₂	83.1	165, 198-200, 242
Hafnocenes (with cyclopentadienyl ligands)		
Me ₂ Si(2,4-Me ₂ Cp) ₂ HfCl ₂	96.8	165, 198-200
Titanocenes (with indenyl ligands)		
En(4,5,6,7-IndH ₄) ₂ TiCl ₂	na	164, 166
En(Ind) ₂ TiCl ₂	na	164, 166
Rac-(C ₃ H ₄ MePh) ₂ ZrCl ₂	na	163,276

na, not available

TABLE 3.7
Selected List of C₅-Symmetric Metallocenes

Metallocenes	Pentad (%)	Ref.
Zirconocenes		
i-Pr(Cp)(Flu)ZrCl ₂	rrr %	
i-Pr(Cp)(Ind)ZrCl ₂	23-95	236,165,198-200,203
t-BuCH(Cp)(Flu)ZrCl ₂	49	165, 198-199
Me ₂ Si(Cp)(4,5-MePh)ZrCl ₂	92-95	199
Ph ₂ C(Cp)(Flu)ZrCl ₂	24	165, 198-199
Me ₂ C(Cp)(Flu)ZrCl ₂	89.5	202
Me ₂ C(Cp)(Ind)ZrCl ₂	83.5	202
[1-(9-Flu)-2-(1-Ind)En]ZrCl ₂	na	165
[1-(9-Flu)-1(R)-Ph-2-(1(R)-Ind)En]ZrCl ₂	na	195
[1-(9-Flu)-1(R)-Ph-2-(1(S)-Ind)En]ZrCl ₂	na	195
i-Pr(Cp)(4,5-MePh)ZrCl ₂ ^a	mmmm, 72	165, 198-199
i-Pr[(MeCp)(Ind)]ZrCl ₂ ^a	mmmm, 54%	165, 198-199
i-Pr[(3-t-BuCp)(Flu)]ZrCl ₂ ^a	mmmm, na	200, 204, 205
Me ₂ Si[(3-t-BuCp)(Flu)]ZrCl ₂	mmmm, na	200, 204, 205
Me ₂ C(MeCp)(Ind)ZrCl ₂ ^a	mmmm, na	165
Me ₂ C(Cp)(2,7-t-Bu ₂ -Flu)ZrCl ₂ ^a	mmmm, na	202
t-BuCH(3-t-Bu-Cp)(Flu)ZrCl ₂ ^a	mmmm, na	200, 204, 205
En(4,5,6,7-IndH ₄) ₂ ZrCl ₂	atactic	178
Hafnocenes		
i-Pr(Cp)(Flu)HfCl ₂	45-52	203

^aC₅-symmetric metallocenes which are isospecific because of the bulky group substitution on the π-carbocyclic ligand. na, not available.

3.3.1. C_{2v} -Symmetric Metallocenes

For the C_{2v} -symmetric metallocene, the polymer tacticity is determined by the chain-end controlled mechanism whereby the configuration of the asymmetric center of the last-inserted prochiral monomer unit dictated the orientation of the next monomer [169, 188-190]. Atactic polypropylene and poly(α -olefin)s are formed because the configuration of the last-inserted monomer unit occasionally changes.

In the presence of MAO, the polymerization or copolymerization activity of Cp_2ZrCl_2 and $CpZrCl_3$ (in the former, the cyclopentadienyl ring is π -bonded with the zirconium; in the latter, it is σ -bonded) is different and varies with the zirconium concentration as well as the aluminum-to zirconium ratio [167]. At the zirconium content of 48 μ mol, the productivity values were comparable. By lowering the concentration 13-fold, the productivity of Cp_2ZrCl_2 increased 17-fold but the corresponding increase for $CpZrCl_3$ was only fivefold. Additionally, the polymerization induction period with $CpZrCl_3$ was longer than with Cp_2ZrCl_2 , whereas its asymptotic polymerization rate was about half the maximum polymerization rate with the Cp_2ZrCl_2 .

Cp_2TiCl_2 and Cp_2HfCl_2 were quite effective in catalyzing the formation of alternating ethylene/propylene copolymers and short block copolymers, respectively [191]. Acyclic 1,3 pentadiene metallocene was also used [192] in polymerizing ethylene in the presence MAO, potassium, titanium tetrachloride, or zirconium tetrachloride but the required cocatalyst-to-catalyst ratio was very high ($10^6:1$).

3.3.2. C_2 - and C_5 -Symmetric Metallocenes

The structural stereorigidity confers a few significant advantages and disadvantages to the C_2 - and C_5 -symmetric metallocenes. The stereorigid zirconocenes, such as $En(Ind)_2ZrCl_2$, $En(IndH_4)_2ZrCl_2$, $rac-En(3-Me_3SiInd)_2ZrCl_2/MAO$, are generally more active [191, 193] in ethylene/propylene

copolymerization than the nonstereorigid varieties such as $\text{Ind}_2\text{ZrCl}_2$, Cp_2ZrCl_2 , Cp_2TiCl_2 , Cp_2HfCl_2 , and Cp_2ZrMe_2 although the copolymer microstructures differ. Conversely, in ethylene polymerization, the catalyst reactivity might suffer [165] because of the stereorigidity of, for example, the C_s -symmetric $\text{rac-i-Pr(Ind)CpZrCl}_2$ versus the C_{2v} -symmetric Cp_2ZrCl_2 .

While the stereorigidity might not always have a positive effect on catalyst activity, symmetry is essentially related to stereospecific polymerization [194, 195]. A chiral catalyst active center, combined with a prochiral propylene or hexene-1 monomer, has a diastereotopic tendency. Stereospecific polymerization could arise either from the chiral β -carbon atom at the terminal monomer unit of the growing chain (i.e., chain end control) or from the chiral catalyst site (i.e., enantiomorphic site control) [170, 178].

The generally accepted mechanism for isospecific polymerization [178, 194, 196-198] of propylene schematically illustrated [171] in Figure 3.17 using, as an example, the active cationic alkylzirconocenium ion generated from a C_2 -symmetric bis(indenyl)zirconocene. The C_2 -symmetric metallocenes [165, 198-200], such as $\text{En(IndH}_4)_2\text{ZrCl}_2$, $\text{En(Ind)}_2\text{HfCl}_2$, $\text{rac-[En(Ind)}_2\text{HfCl}_2$, $\text{Et}_2\text{Si(3-MeCp)}_2\text{ZrCl}_2$, $\text{rac-Me}_2\text{Si(Ind)}_2\text{HfCl}_2$, and $\text{rac-Me}_2\text{Si(2,4-Me}_2\text{Cp)}_2\text{HfCl}_2$, possess homotopic coordination sites which favor identical orientation of the approaching prochiral monomer resulting in isospecific polymerization. Stereospecificity is also temperature-dependent as illustrated [195] with the C_2 -symmetric $\text{PhEn(1,2-Flu)}_2\text{ZrCl}_2$.

Syndiospecific propylene polymerization normally results from the use of C_s -symmetric prochiral metallocenes because of the enantiotopic vacant coordination site, regenerated by the chain migration [198, 201, 202], which ensures that the incoming olefin asymmetric carbon atoms follow each other alternately and regularly [197, 203, 204]. The stereospecificity of chiral titanocene and zirconocene arises from the enantiomorphic site control mechanism.

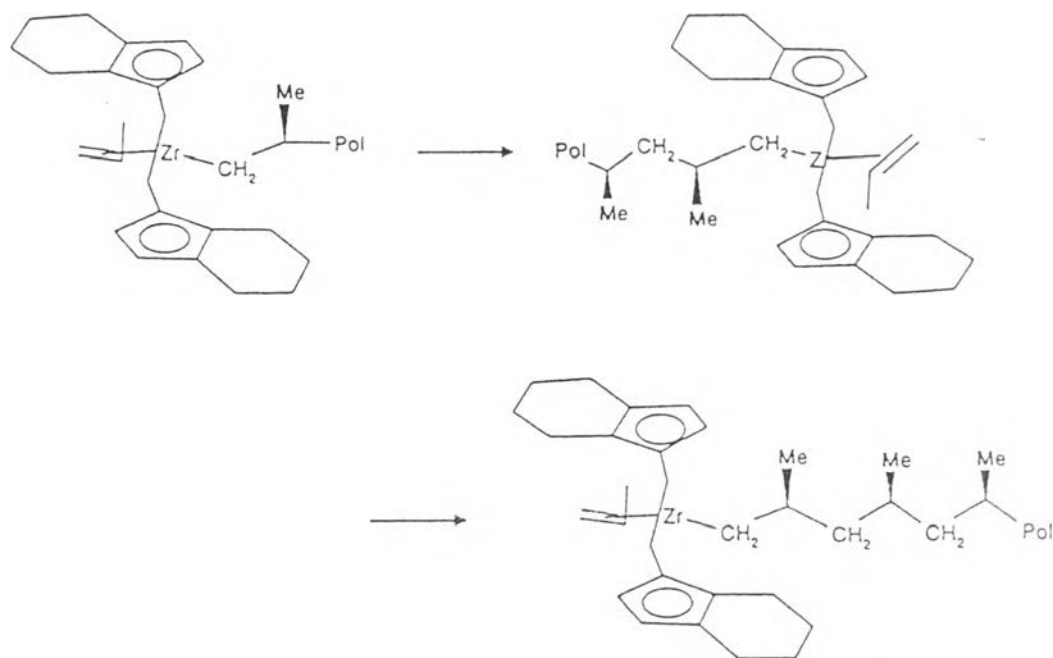


Figure 3.17. Schematic illustration of isospecific polymerization of propylene using cationic alkylmetallocenium active site generated from a C_2 -symmetric with bis(indenyl)zirconocene [171].

The C_s -symmetric metallocenes [165, 198, 199], such as $i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$, $i\text{-Pr}(\text{Cp})(4,5\text{-MePh})\text{ZrCl}_2$, $\text{Me}_2\text{Si}(\text{Cp})(4,5\text{-MePh})(\text{ZrCl}_2)$, $\text{rac-[}i\text{-Pr}(\text{Ind})(\text{MeCp})\text{]ZrCl}_2$, and $\text{rac-}i\text{-Pr}(\text{Cp})(\text{Ind})\text{ZrCl}_2$, favor syndiospecific polymerization because of the enantiotopic vacancies formed by the chain migratory insertion. If, however, the π -carbocyclic ligand used in the metallocene has substituents at key positions, isospecific polymerization of propylene could occur owing to the steric hindrance of the π -ligands which blocks the approaching propylene monomer. This is exemplified by the *t*-butyl group substitution at distal 3-position in the cyclopentadienyl ligand which results in the following isospecific C_s -symmetric metallocenes [200, 204, 205]: $t\text{-BuCH}(3\text{-}t\text{-Bu-Cp})(\text{Flu})\text{ZrCl}_2$, $\text{Me}_2\text{Si}[(3\text{-}t\text{-Bu-Cp})(\text{Flu})]\text{ZrCl}_2$ and $i\text{-Pr}[(3\text{-}t\text{-Bu-Cp})(\text{Flu})]\text{ZrCl}_2$. While both the syndiotactic and

isotactic polypropylenes are crystalline, stereospecific polyhexene, resulting from the prochiral hexene-1, is amorphous.

3.4. Variation of Bridging Moieties

The presence of different bridging moieties on a metallocene has electronic and steric implications [205] and would therefore affect catalyst reactivity, polymer molecular weight characteristics, the comonomer incorporation capability, and polymer microstructure. Some interesting investigations include the use of diphenylmethylene and phenylmethylmethylene bridging moieties as well as the use [165] of silyl and alkyl/aryl groups such as Me_2Si , Ph_2Si , and Bz_2Si for the C_s -symmetric, prochiral zirconocene, and hafnocene dichlorides [206, 207]. Two examples of the bridged metallocenes are as follows [205]: $\text{rac-Me}_2\text{EnMe}_2(2\text{-H-4-t-BuCp})_2\text{ZrCl}_2$ and $\text{rac-Me}_2\text{Si}(2\text{-H-4-t-BuCp})_2\text{ZrCl}_2$. In certain specific C_s -symmetric zirconocenes, such as $\text{rac-[1-(9-Flu)-2-(1-Ind)En]ZrCl}_2$, the conformation of the alkene-containing bridge could be changed through phenyl substitution resulting in the following diastereomers: $\text{rac-[1(9-Flu)-1(R)-Ph-2-(1(R)-Ind)En]ZrCl}_2$ and $\text{rac-[1-(9-Flu)-1(R)-Ph-2-(1(S)-Ind)En]ZrCl}_2$ with δ -forward and λ -backward conformations, respectively. The two are characterized by different stereospecificity [195].

The use of different bridging moieties, coupled with different π -ligands, not only affects catalyst reactivity and polymer molecular weight characteristics, it also affects the comonomer incorporation capability during the ethylene/hexene-1 copolymerization[208]. Zirconocenes so modified [236, 208, 209] are C_s -symmetric $i\text{-Pr(Flu)(Cp)ZrCl}_2$, and C_2 -symmetric $\text{Me}_2\text{Si(Ind)}_2\text{ZrCl}_2$, $\text{En(IndH}_4)_2\text{ZrCl}_2$, $\text{Ph}_2\text{Si(Ind)}_2\text{ZrCl}_2$, $\text{Bz}_2\text{Si(Ind)}_2\text{ZrCl}_2$, and $\text{rac-En(Ind)}_2\text{ZrCl}_2$. The difference in the observed catalytic activity, comonomer incorporation capability, and resulting polymer microstructure resulting from $\text{rac-En(Ind)}_2\text{ZrCl}_2$ and $\text{rac-En(Ind)}_2\text{HfCl}_2$ is attributable to their ligand-metal distances[210].

The emergence of monocyclopentadienyl metallocene, whereby one ring is replaced with a heteroatom that is attached to the bridging atom, created some excitement. This is exemplified by $\text{Me}_2\text{Si}(\text{Me}_4\text{Cp})(\text{t-Bu-N})\text{ZrCl}_2$ where the heteroatom, N, is σ -bonded directly to the transition metal [211-215]. In the presence of MAO as a cocatalyst, it was effective in ethylene homopolymerization and copolymerization with high molecular weight and low polydispersity index. This type of metallocene has already assumed some industrial [214, 215] significance and a recent catalyst system for the ethylene homo- and copolymerization, due to DOW [214], consists of a substituted cyclopentadienyl, a dimethylsilyl with a nitrogen bridge to the titaniumdichloride, $\text{Me}_2\text{Si}(\text{Me}_5\text{Cp})(\text{Me-N})\text{TiCl}_2$.

Two different classes of polymeric materials, namely, elastomers and polyolefin elastomers, have resulted from the ethylene/octene-1 copolymerization using this monocyclopentadienyl metallocene catalyst. The first contains up to 20wt% octene-1, is flexible, and has properties similar to these of conventional LLDPE and VLDPE at much lower densities. The second contains more than 20 wt% octene-1 and is characterized by a measure of flexibility, clarity, and tensile strength that make it suitable for applications previously dominated by such flexible thermoplastics as plasticized PVC, EVA copolymer, EMA copolymer, styrene block copolymers, EPR, and EPDM [171, 216].

3.5. Variation of π -ligands

The catalyst activity, stereospecificity, comonomer incorporation capability, and the resulting polymer molecular weight characteristics are also dependent on the carbocyclic π -ligands [165, 208]. The zirconocene based on indenyl, $(\text{Ind})_2\text{ZrMe}_2$, showed remarkably higher activity than the corresponding zirconocene based on Cp, Cp_2ZrMe_2 . Although the activity was solvent-dependent, the indenyl ligand complexes being more active in toluene than in heptane [217], the overall effects of changing the π -ligand on the activity of the chloride-free zirconocene catalyst systems are in the following order: $(\text{Ind})_2 > \text{Cp}_2$

The C_5 -symmetric $i\text{-Pr}(\text{Cp})(\text{Flu})\text{ZrCl}_2$ forms syndiotactic poly(hexene-1) and incorporates far more hexene-1 when used in ethylene/hexene-1 copolymerization. The C_2 -symmetric $\text{En}(\text{IndH}_4)_2\text{ZrCl}_2$ forms isotactic poly(hexene-1) and incorporates a moderate amount of hexene-1 when used in ethylene/hexene-1 copolymerization [208-210, 218]. The C_{2v} -symmetric Cp_2ZrCl_2 forms atactic poly(hexene-1) and incorporates far less hexene-1 when used in ethylene/hexene-1 copolymerization. This observed effect could be enhanced when combined with the variation of the cocatalyst-to-catalyst ratio as illustrated [236] with $\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$ and $i\text{-Pr}(\text{Flu})(\text{Cp})\text{ZrCl}_2$.

On replacing the Cp with bis(neomethyl- η^5 -cyclopentadienyl) and testing the resulting $(n\text{-MeCp})_2\text{ZrCl}_2/\text{MAO}$ system, the polymerization rate, catalyst induction period, and catalyst deactivation were affected owing to the electronic and steric effects [219]. Single alkyl substituents on each Cp increases polyethylene formation possibly because of electron donation enhancement of the coordinated anionic propagation. The substituent size effects are opposite and similar results have been obtained by different investigators [181, 220-223]. The use of other substituents decreased the catalytic activity of copolymerizing ethylene and hexene-1 in the following order: $\text{Me}_2\text{Si}(\text{Cp}) > n\text{-BuCp} \approx \text{Cp}$, and this is also explainable in terms of electron effect. However, the weight-average molecular weight decreased in [224] the order of $n\text{-BuCp} > \text{Cp} > \text{Me}_2\text{Si}(\text{Cp})$.

For bridged metallocenes with the cyclopentadienyl ligands, stereospecificity is substantially controlled by the substituents in the β position of the cyclopentadienyl ligands. Indeed, substitutions on any carbocyclic π -ligands could affect catalyst activity, kinetic profile, molecular weight characteristics, comonomer incorporation capability, and the resulting polymer microstructure.

This is exemplified by the following: (1) the alkyl group substitutions [225] at positions 2 and 4 of the indenyl ligand in $\text{Me}_2\text{Si}[\text{Ind}]_2\text{ZrCl}_2$; (2) the alkyl group substitutions [205] at positions 2(H, Me) and 4 (t-Bu, i-Pr) of the cyclopentadienyl ligand in $\text{Me}_2\text{Si}[\text{Cp}]_2\text{ZrCl}_2$; (3) the substitutions [179] of benzene and

2-methylbenzene in the β -position of the indenyl ligand to give $\text{Me}_2\text{Si}[\text{BenzInd}]_2\text{ZrCl}_2$, $\text{Me}_2\text{Si}[2\text{-MeBenzInd}]_2\text{ZrCl}_2$, or $\text{Me}_2\text{Si}[2\text{-MeInd}]_2\text{ZrCl}_2$; (4) the substitutions [221] of electron acceptors/donors at positions 4 and 7 or 5 and 6 of indenyl ligand in $\text{Ind}_2\text{ZrBz}_2$; (5) the substitutions [222] of H, Me, or OMe at positions 5 and 6 of indenyl ligand to give chiral $\text{En}[5,6\text{-H}_2\text{Ind}]_2\text{ZrCl}_2$, $\text{En}[5,6\text{-MeInd}]_2\text{ZrCl}_2$, and $\text{En}[5,6\text{-OMeInd}]_2\text{ZrCl}_2$; and achiral $[5,6\text{-H}_2\text{Ind}]_2\text{ZrCl}_2$, $[5,6\text{-MeInd}]_2\text{ZrCl}_2$, $[5,6\text{-OMeInd}]_2\text{ZrCl}_2$, and $[5,6\text{-Cl}_2\text{Ind}]_2\text{ZrCl}_2$; and (6) the substitutions [220] of SiMe at position 3 of cyclopentadienyl in zirconocene dichloride bridged with either a nitrogen-free aromatic/aliphatic moiety or a nitrogen-containing aromatic/aliphatic moiety.

The molecular weight dependence is related to the electronic (and steric) effects on chain propagation and termination mechanisms [187, 203, 226]. This is possibly due to the electron-releasing substituent, which lowers the Lewis acidity of the active cationic alkylmetallocenium ion and thereby reduces its tendency for termination via the β -hydride elimination mechanisms [167, 203, 225]. Generally, the electron-donating aryl substituents are more effective than the alkyl analogues in stabilizing the active cationic species [222], and some effective methods have been developed for introducing aromatic substituents on, for example, the π -ligands of the chiral C_2 -symmetric zirconocene dichloride having the Me_2Si bridging moiety [227]. The protruding ligand framework constitutes a steric hindrance for the bulky monomer as it approaches the transition metal center; it also influences the resolution of the competition between termination and propagation, which dictated the polymer molecular weight characteristics. The catalyst stability has also been related to the inherent steric hindrance of the protruding ligand framework.

When hydrogen is used for controlling the molecular weight of metallocene polyolefins, the terminal unsaturation becomes saturated, and the site available for building functionalities in the polymer is lost. In the study of the role of π -ligand in controlling the molecular weight in the absence of hydrogen, the alkyl-substituted cyclopentadiene was found to be effective [166, 228]. The mono-methyl-substituted cyclopentadienyl, with increased electron density at the metal center and relatively

little opposing steric effects on ethylene coordination, was more active and gave a higher molecular weight than the other alkyl substituent.

3.6. Cocatalysts and Modifiers

The key factor for the high activity for the metallocene catalyst systems is the cocatalyst methylaluminumoxane whose involvement is crucial in the formation of the metallocene active species. Polymerization kinetic profile, stereospecificity, comonomer incorporation as well as the resulting polyolefins' molecular weight characteristics are affected not only by the amount of MAO used, but also by the metallocenes/MAO ratios. A strong effect on the polymerization kinetic profile was demonstrated for the following: $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, $\text{Cp}_2\text{TiEnCl}/\text{AlEtCl}_2$ [162], $\text{Cp}_2\text{TiEnCl}/\text{AlMe}(\text{BHT})_2$ [231, 232]. Trimethylaluminum (TMA), an alkylating agent that is also a scavenger, was used with these catalysts.

Zirconocenes in the presence of TMA show limited polymerization activity [162, 233], whereas methylaluminumoxane increases [261] the activity by a factor of 10^5 . Indeed, the influence of different aluminumoxane cocatalyst type on the activity of Cp_2ZrMe_2 and Cp_2ZrCl_2 catalysts is in the following order [217]:

Methylaluminumoxane > triisobutylaluminumoxane > ethylaluminumoxane.

The value of the cocatalyst (MAO)-to-catalyst ratio is important. An unusually high value of 5×10^4 to 1 has been used to achieve high activity in homogeneous catalysis regardless of the π -ligand type. Polymer properties such as molecular weight distribution and density are influenced by this ratio for the following metallocenes [176, 167, 219, 230, 259]: CpZrCl_3 , Cp_2ZrCl_2 , Cp_2ZrMe_2 and $(n\text{-MeCp})_2\text{ZrCl}_2$.

For propylene polymerization, the activity appears to be an increasing function of the $[\text{Al}]:[\text{Zr}]$ molar ratios up to a point, for $\text{rac-En}(\text{Ind})_2\text{ZrCl}_2/\text{MAO}$,

rac-En(4,5,6,7-IndH₄)₂ZrCl₂/MAO [234, 235], and (n-MeCp)₂ZrCl₂/MAO [219]. Very high [Al]:[Zr] molar ratios are also needed for ethylene polymerization for prochiral i-Pr(Flu)(Cp)ZrCl₂ and chiral Me₂Si(Ind)₂ZrCl₂ [236]. In contrast, a lower cocatalyst-to-catalyst ratio enhances the activity of the monocyclopentadienyl metallocene, namely Me₂Si(Me₄Cp)(t-Bu-N)ZrCl₂ in ethylene polymerization [215]. The dependence of the catalytic activity on the [Al]:[Zr] ratio has been attributed to the rapid association-dissociation equilibria of MAO involving acid-base and/or electron deficient bridge complexation.

The use of solid reaction product of (Me₅Cp)₂ZrCl₂, (Me₅Cp)₂ZrMe₂, or (n-BuCp)₂ZrCl₂, in excess methylaluminumoxane facilitates the reduction of the high cocatalyst-to-catalyst ratio [237, 238]. It was shown that the use of TMA in combination with MAO was effective aside from the fact that the replacement of MAO with a substantial amount of TMA minimizes the potential hazards of MAO synthesis. However, the molar ratio of TMA:MAO becomes an additional parameter whose value influences the catalyst activity, polymerization kinetic profile, and polyethylene properties, depending on the π -carbocyclic and σ -hydrocarbyl ligands [230] or the level of dilution of TMA with its sterically hindered aryloxy derivative [232]. Similar studies were carried out using chloride-free Cp₂ZrHex₂ and Ind₂ZrMe₂ systems differing results[239].

Preactivation of metallocene precursor with the methylaluminumoxane also affects catalyst activity, comonomer incorporation, as well as polyolefins microstructures as demonstrated, in propylene homo- and co-polymerization (ethylene/propylene or α -olefin/propylene), with the following metallocene catalysts: Me₂Si(Ind)₂ZrCl₂ [240, 241]; En(Ind)₂HfCl₂, Me₂Si(Ind)₂HfCl₂ [242]; rac-En(Ind)₂HfCl₂ [206, 242]; Ph₂Si(Ind)₂ZrCl₂, MePhSi(Ind)₂ZrCl₂, En(Ind)₂ZrCl₂, i-Pr(Ind)₂ZrCl₂, and En(3-Me₃Si(Ind)₂ZrCl₂ [193, 227, 240, 241]; rac-Me₂Si(Ind)₂HfCl₂ [242]; Me₂Si(Me₄Cp)(t-Bu-N)ZrCl₂ [215].

3.6.1. Lewis Acids

Lewis acids, in combination with an alkylating agent or a scavenger such as TMA, could be effectively used as cocatalysts with the metallocene catalysts for olefin homo- and copolymerization. The Lewis acids that have been used include Me_2AlF [243], $[\text{B}(\text{C}_6\text{H}_5)_4]^-$ [244], $[\text{B}(\text{C}_6\text{F}_5)_3]$ [245], $[\text{C}_2\text{B}_9\text{H}_{12}]^{2-}$ [246], $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ [203, 247], $[\text{R}_2\text{R}'\text{NH}][\text{B}(\text{C}_6\text{F}_5)_4]$ [248], and $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_4(\text{SiR}_3))]$ [249]. To polymerize ethylene, Lewis acid such as *N,N*-dimethylanilinium tetrakis(pentafluorophenyl)borate (AFPB) and tris(pentafluorophenyl)boron were used separately, or mixed with trimethylaluminum as cocatalyst plus monocyclopentadienyl derivatives and homoleptic hydrocarbyls of titanium and zirconium [250, 251]. With AFPB, the catalytic activity was comparable to that shown with MAO, even at low dosage. Likewise, a mixture of varying proportions of trimethylaluminum and $\text{Me}_2\text{AlF}(\text{DMF})$ has been used to polymerize olefin without MAO [242].

Ethylene could also be polymerized [252, 253] in toluene using $(\text{Me}_5\text{Cp})_2\text{ZrMe}_2$ reacted with tributylammonium salts of para-substituted tetraarylborates, $\{[\text{BuN}_3\text{H}][\text{B}(\text{C}_6\text{H}_4\text{R})_4]\}$, where $\text{R} = \text{H}, \text{Me}, \text{and Et}$. This is an ionic, base-free zirconocene catalyst that uses neither the pyrophoric alkyl aluminum nor an excess amount of MAO. Generally, noncoordinating anions, such as fluorinated boron together with metallocenes, form ion pairs, which are not stable [170, 254] at polymerization temperature above 60°C . Strong Lewis acid additives [204, 247, 255] such as $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ and $[\text{B}(\text{C}_6\text{F}_5)_3]$ could be used alkyl aluminum cocatalysts and $(\text{MeCp})\text{TiCl}_3$ catalyst to polymerize propylene or for ethylene/propylene copolymerization. The resulting polypropylene is atactic, and the copolymer is random having a structure similar to that produced with homogeneous vanadium catalyst system.

3.6.2. Miscellaneous Additives

For polymerization and ethylene/hexene-1 copolymerization, tetramethyl silicate and silane additives enabled [266] the formation of polyethylenes with low melt flow rate over a sufficiently high temperature range with a variety of metallocene catalyst systems, namely, $\text{Cp}_2\text{ZrCl}_2/\text{MAO}$, $\text{Cp}_2\text{ZrMeCl}/\text{MAO}$, and $\text{Ind}_2\text{ZrCl}_2/\text{MAO}$. The polymerization could take place at a temperature higher than the melting point of the product, making it possible for a direct introduction of the as-polymerized molten polymer into the extruder for pelletizing. The solid reaction product of butyl octyl magnesium and silicon or tin tetrachloride was also effective [256, 257]. The use of trimethyl boroxine, a scavenger for chain transfer agent, with Cp_2ZrCl_2 , prior to the addition of MAO, increased the polypropylene productivity significantly. The effect was different for $\text{rac-En}(4,5,6,7\text{-IndH}_4)_2\text{ZrCl}_2$ or $\text{rac-En}(\text{Ind})_2\text{ZrCl}_2$ where the productivity benefit is possible only if the catalyst is pretreated with boroxine [258].

The magnitude of cocatalyst (MAO)-to-catalyst ratio, as well as the content of the Lewis acid catalyst modifiers, influences the catalyst activity, polymerization kinetic profile, and polypropylene microstructure for the C_2 -symmetric [233, 234] $\text{rac-En}(\text{Ind})_2\text{ZrCl}_2$ and $\text{rac-En}(\text{IndH}_4)_2\text{ZrCl}_2$ as observed before for the C_{2v} -symmetric metallocenes [167, 219, 230].

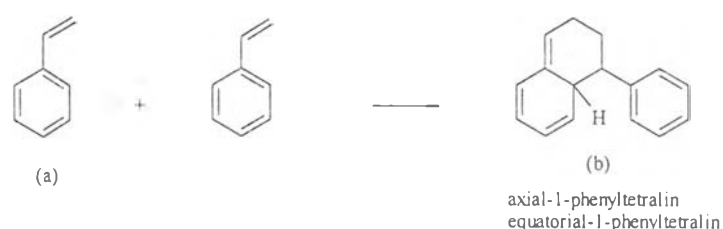
3.7. Styrene polymerization [277]

Styrene is slightly polar compared to ethylene and α -olefins. The lack of a strongly polar functional group allow styrene to undergo highly (>95-98%) isospecific polymerization with many of the heterogeneous Ziegler-Natta initiators effective for α -olefins [Iongo et al., 1990; Pasquon et al., 1989; Soga et al., 1988]. Highly syndiotactic polystyrene is obtained using soluble Ziegler-Natta initiators, such as tetrabenzyltitanium, tetrabenzylzirconium, and tetraethoxytitanium or cyclopentadienyltitaniumtrichloride with methylaluminumoxane [Ishihara et al., 1988; Pellecchia et al., 1987; Zambelli et al., 1989]. Further, there are recent reports of

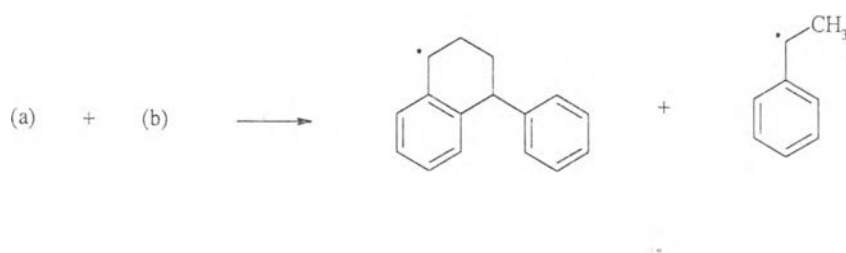
highly syndiospecific polymerizations of styrene with heterogeneous initiators based on tetra-n-butoxytitanium and methylaluminoxane supported on silica or magnesium hydroxide [Soga and Monoi, 1990; Soga and Nakatani, 1990]. Styrene can also be homogeneously polymerized. The C-C double bond of styrene can act either as electron-donating or as electron-withdrawing center. Therefore, not only radicals can polymerize styrene but also anionically or cationically or by Ziegler-Natta initiators.

3.7.1. Radical Polymerization

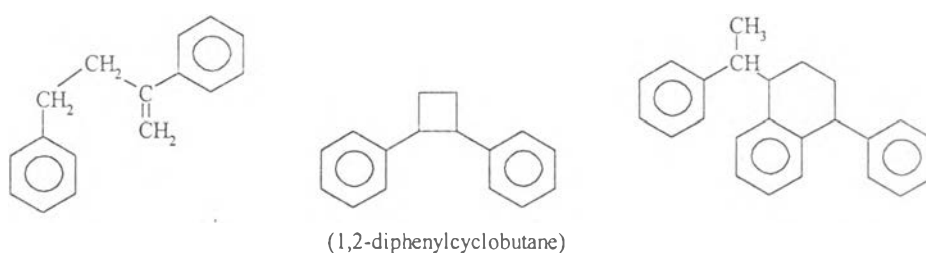
Styrene can be polymerized without a chemical initiator simply by heating. The first step is a Diels-Alder reaction:



Only the axial isomer can react with a further styrene atom, yielding two radicals, which can start a radical polymerization:



Some of the possible dimers and the trimer have been identified:



Initiators: The list of initiators available for radical polymerization of styrene is very long. An interesting development is the application of initiators like



which decompose to form four radicals. It is even more interesting to have a different half-life for both peroxide groups. This presents novel opportunities for changing the molecular weight and its distribution.

Inhibitors: During shipping and storage styrene needs an inhibitor. The most efficient inhibitors--quinones, hindered phenols, and amines--require traces of oxygen to function. t-Butyl-catechol at 15 to 50 ppm is the most common inhibitor for commercial styrene. It is also possible to use nitrophenol, hydroxylamine, and nitrogen oxide compounds. To avoid an induction period, the inhibitors have to be removed before polymerization. Traces of metal such as iron or copper and sulfur compounds are the cause of retardation effects.

Chain transfer: In styrene polymerization the chain transfer agent can be the solvent, monomer, initiator, polymer, or an added chemical agent. As $C_{tr} = k_p/k_{tr}$ increases, the chain transfer agent becomes more effective. The most important property affected by chain transfer is the molecular weight of the polymer. The transfer to monomer has a value of 10^{-5} which can be neglected. However, since the transfer constant to the Diels-Alder dimer equatorial 1-phenyltetralin is about 118 at 80°C , this may cause experimental error. Any transfer to polymer would lead to branched structures in the final product. Although this reaction has been investigated to some extent, there is no conclusive evidence that it is an important reaction. The most important aspect of chain transfer is the control of molecular weight by the adequate use of added transfer agent. Mercaptanes are by far the most widely used chemicals for this purpose.

Termination reactions: The free radical polymerization of styrene is terminated almost exclusively by the combination of two growing chains:



Termination is diffusion controlled at all temperatures below 150°C. Increasing viscosity leads to a reduction in the termination rate. However, the resulting Trommsdorff effect is comparably small for polystyrene.

Processing: Free-radical polystyrene can be synthesized either by bulk, solution, suspension, or emulsion techniques. The bulk process needs pure styrene; it is very simple and yields polymer with high clarity. Due to its poor control, this process is not used commercially. In solution polymerization styrene is diluted with solvents, which makes temperature control easier. However, solvents normally reduce the molecular weight and polymerization rate. Both processes can be carried out either in batch or continuously. The advantages are more uniform products and low volatile levels. The main disadvantage is the transportation of highly viscous finished product.

Suspension polymerization is still an important mode of polystyrene production, although it has lost ground to continuous solution polymerization. The polymerization system contains monomer suspended in water, stabilizing agents, and initiators to speed polymerization. The easy heat control and removal of the finished polymer count as advantages. Contamination with stabilizing agents is considered a disadvantage.

Emulsion polymerization requires water as a carrier with emulsifying agents. It yields extremely small particles. Advantages are rapid reactions and excellent heat control. Disadvantages are the contamination of polymer with the emulsifier, water, its deficit in clarity, and the limitation to batch processing. However, this type of processing is important for ABS polymers.

3.7.2. Anionic Polymerization

The phenyl group of styrene is able to act as an electron-donating or an electron-withdrawing center. This situation allows the growing end of the polymer to be either a carbeniumion or a carbanion. It also makes it possible to polymerize styrene by Ziegler-Natta catalysts.

Initiation: A highly purified monomer is reacted with a strong base. Although several initiators are known, organolithium compounds are the most studied and probably the best understood initiators.



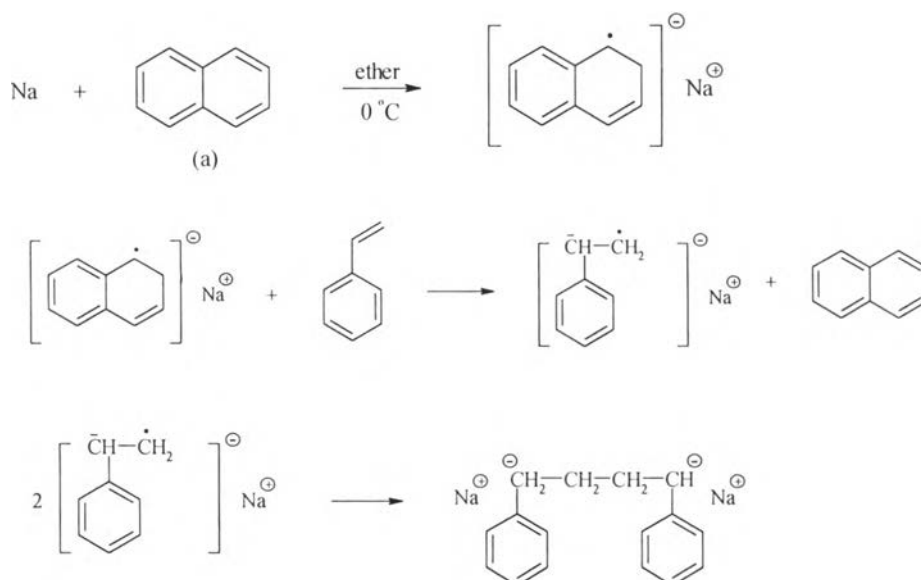
Propagation: The anionic chain end then propagates the chain by adding another monomer molecule.

The ideal polymerization of this type obeys the following equation:

$$R_p = k_p [C^*] [M]$$

where C^* represents the molar concentration of active chain ends. The rate constant is strongly affected by the solvent. In addition to solvent, the counterion affects the rate of polymerization. The effect of the counterions is often explained on the basis of their sizes. For the growing end of poly(styryllithium), an association of two growing chains has been discussed. This complex dissociates if polar solvents such as THF and ethyl ether are added, resulting in an increase in the polymerization rate. Instead of using a monofunctional initiator, it is possible to use a bifunctional anionic initiator. One of the best described systems involves the reaction between

metal and naphthalene, forming a radical anion that transfers this character to the monomer; the two radical anions combine quickly to form a dianion.



3.7.3. Cationic Polymerization

The commercial use of cationic polymerization of styrene is practically nonexistent at this time because of the low temperature needed, uncontrollable molecular weight, and residual acidic initiator. However, since numerous basic papers are published on this topic it is discussed here briefly. The initiators of a cationic polymerization of styrene can be carried out in the presence of strong acids like: protonic acids like perchloric, hydrochloric or sulfuric acid or Lewis acids. Additionally, alumina, silica, and molecular sieves were used to initiate cationic polymerization.

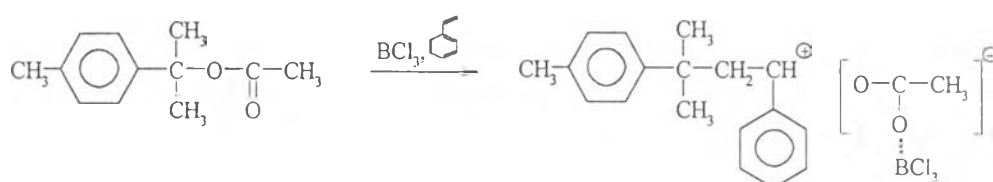
Cationic polymerization of styrene in the presence of salts such as $(n\text{-Bu})_4\text{N}^+\text{ClO}_4^-$ has been shown to accelerate the polymerization rate compared to the

rate for salt-free polymerization. This result is explained on the basis of the following reaction:

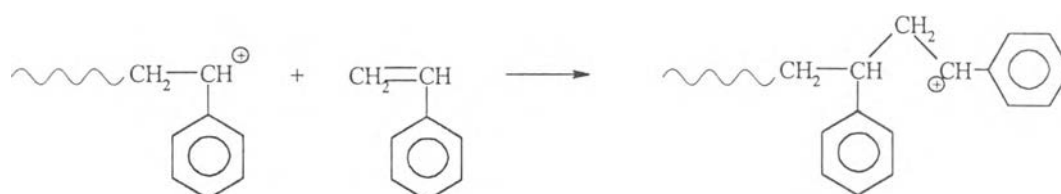


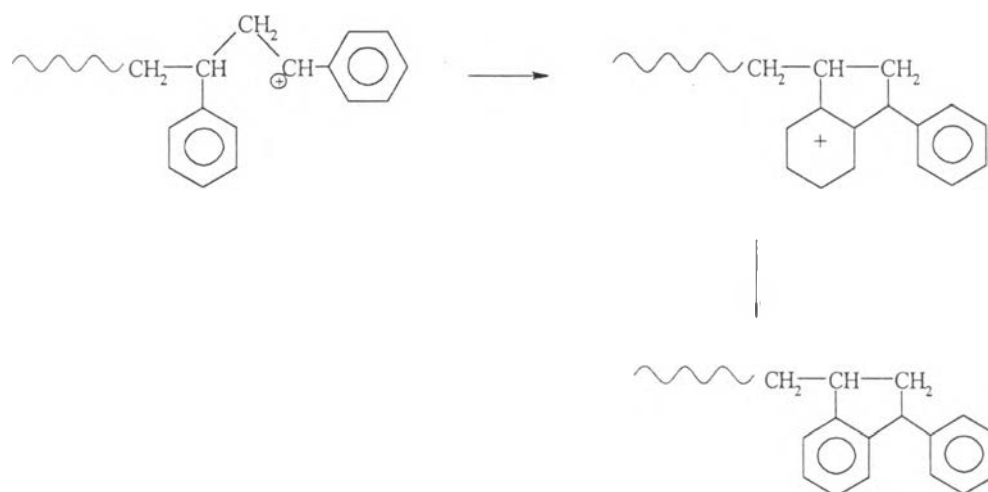
Interesting effects were observed if cationic polymerization was carried out under an electric field. Depending on the solvent, the degree of ion separation is decreased under the influence of the electrical field. However, if toluene is applied, the effect is small due to the low ϵ value of the solvent. In the range of intermediate values of ϵ (dichloroethane) the highest changes in rate are observed. In nitrobenzene, a solvent with high ϵ values, the ion separation is almost complete. Therefore, application of an external field does not affect the free ion concentration and the rate.

Normally, molecular weight is difficult to control in cationic polymerization of styrene. This is not only because of transfer to polymer and solvent but also of transfer to monomer. Friedel-Crafts reactions during growth with aromatic solvents significantly decrease the molecular weight.



Addition of further monomer results in an increase in molecular weight. The danger of termination by indane formation seems to be reduced by adding the monomer in small portions:





3.7.4. Coordination Polymerization

Styrene can be polymerized to stereoregular by coordination catalysts. Highly isotactic polystyrene is prepared using catalysts obtained from the reaction between TiCl_4 and AlEt_3 and of a $\text{TiCl}_3/\text{Al}(\text{i-Bu})_3$ mixture. Optimal conditions for isotactic structures are 0 to 10°C , with aging for at least 10 min but no longer than 30 min. Furthermore, the Al/Ti ratio has to be 3:1 for the formation of isotactic polystyrene. A mixture of methylaluminoxane and tetrabenzyltitanium was used as catalyst.