CHAPTER II
LITERATURE REVIEWS

2.1 Ziegler-Natta Catalysts

2.1.1 The Composition of Ziegler-Natta Catalysts

Generally speaking, the Ziegler-Natta catalyst is a complex formed by reaction of a transition metal compound (halide, or alkoxide, or alkyl or aryl derivative) of group IV-VIII transition metals with a metal alkyl or alkyl halide of Group I-III base metals[2]. The former component is usually called the catalyst and the latter the cocatalyst. There are a very large number of patents involving every combination of pure or mixed metal alkyls with transition metal compounds, each claiming particular advantages. In practice, only a few group I-III metal alkyls are effective. Aluminum alkyls (such as $AlEt_3$, Al-i-Bu_3, $AlEt_2Cl$, $AlEtCl_2$ and $AlEt_2OR$) have been overwhelmingly preferred[3]. Also, transition metal compounds containing titanium (Ti), vanadium (V), chromium (Cr) and, in special cases, molybdenum (Mo), cobalt (Co), rhodium (Rh) and nickel (Ni) are primarily used.

Not long after Ziegler-Natta catalysts were discovered, it was found that electron donors could greatly affect the catalyst's kinetic and stereochemical behavior. Electron donor compounds, such as amines, ethers and esters, have the potential of complexing and reacting with the components of the catalyst or the active centers. They have been used in controlled amounts in many Ziegler-Natta catalytic systems as a third component to increase catalyst activity and/or stereoselectivity[1].

2.1.2 Stereospecificity

Stereochemical control is one of the most important attributes of the Ziegler-Natta catalyst.

2.1.2.1 Steric Isomerism and Tacticity

Steric isomerism is observed in the polymerization of alkenes whenever one of the carbon atoms of the double bond is at least monosubstituted. The polymerization of a monosubstituted ethylene, $CH_2=CHR$ (where R is any substituent group), leads to polymers in which every other carbon atom in the polymer chain is a pseudochiral center. Each pseudochiral center is a site of steric isomerism in the polymerization of $CH_2=CHR$. Considering the main carbon-carbon chain of the polymer $-(C_2-CHR)n-$ to be stretched out in its fully extended planar zigzag conformation, two different configurations are possible for each pseudochiral carbon since the R group may be situated on either side of the plane[4].

The regularity in the configuration of successive pseudochiral centers determines the overall order of tacticity of the polymer chain. If the R groups on successive pseudochiral carbons are randomly distributed on the two sides of the planar zigzag polymer main chain, the polymer is termed atactic. An isotactic polymer structure occurs when the pseudochiral center in each repeating unit in the polymer chain has the same configuration. In this case, all the R groups will be located on one side of the plane of the carbon-carbon polymer chain. A syndiotactic polymer structure occurs when the configuration of the pseudochiral centers alternate from one repeating unit to the next with the R groups located alternately on the opposite sides of the polymer chain plane.[4] (see Figure 2.1). For polymerizations of 1,2-disubstituted ethylene and dienes, steric isomerism is quite complicated.

2.1.2.2 Stereochemical Control by Ziegler-Natta Catalysts

Ziegler-Natta catalysts provided for the first time stereochemical control of the polymerization process. By carefully selecting the combination of catalyst and cocatalyst, one is able to produce polymers with the desired steric structure.

The polyethylene produced in Ziegler-Natta polymerization is linear, which is characterized by the absence of long or short chain branching. For α-olefin polymerization, polyolefins of isotactic or syndiotactic structure can be obtained by using special Ziegler-Natta catalysts. There are even more choices in steric structures for polydienes; polydienes of the *1,4-cis-*, the *1,4-trans-*, and the 1,2-structure, as well as the 3,4-structure in the case of substituted dienes, can be produced with proper Ziegler-Natta catalysts[5].

2.1.3 The Mechanism of Ziegler-Natta Polymerization

2.1.3.1 The Cossee Mechanism

Cossee proposed a monometallic mechanism for Ziegler-Natta olefin polymerization in the 1960s and the following concepts of this proposal have been generally accepted.[1,2,6]

The Active Center - The active center in Ziegler-Natta catalysts is the transition metal-carbon bond of the transition metal complex, which is formed by the interaction between two components of the catalytic system. The active complex has to contain at least one MT-C bond or MT-H bond (MT: transition metal). Furthermore, an open coordination place must be present or formed during the reaction.

Two-Step Mechanism - Polymerization takes place by two steps: (1) complexation of the monomer to the transition metal atom of the active center; (2) migratory insertion of the complexed monomer to the bond between the transition metal atom and first carbon atom of the polymer chain. Repetition of the processes is responsible for the chain growth.
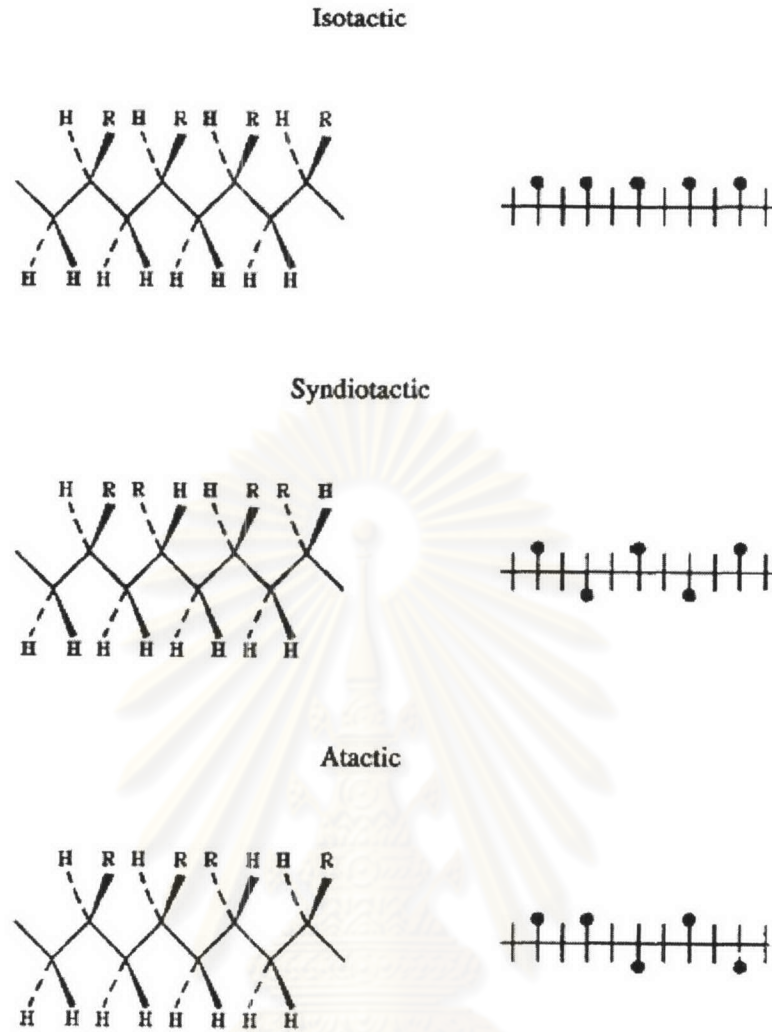
Isotactic

Syndiotactic

Atactic

Figure 2.1 The steric isomers of monosubstituted alkenes [4]

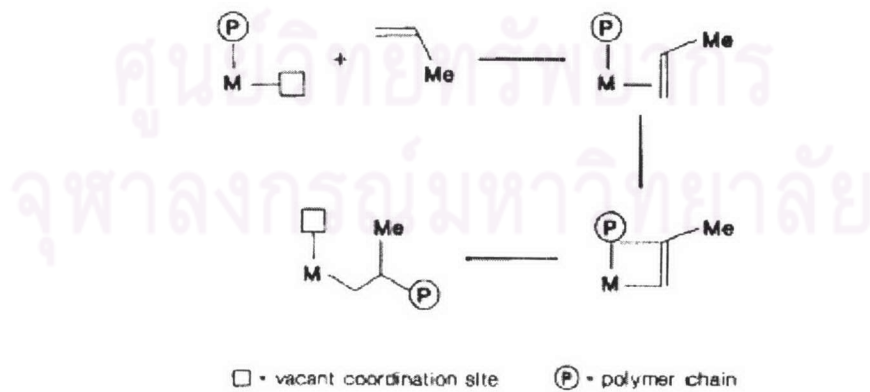□ · vacant coordination site   Ⓟ · polymer chain

Figure 2.2 Cossee mechanism for Ziegler-Natta olefin polymerization [7]

In the Cossee mechanism (see Figure 2.2), a vacant coordination site is generated initially, followed by olefin complexation. Formal migration of the polymer chain, P, and formation of the metal-carbon bond occur concertedly through a four-center transition state. This recreates a vacant coordination site at the site originally occupied by the polymer chain and the process continues; the growing polymer chain terminus flips from site to site.[7]

2.1.3.2 Chain Termination

The termination of the growing chain is mostly caused by chain transfer reactions, including transfer to monomer, to metal alkyls and to the transfer agent, and also caused by thermal cleavage of the active center involving (β-hydrogen elimination. In many cases, a transfer agent, such as H_2, is deliberately introduced into the polymerization system for control of the molecular weight of the product. Figure 2.3 shows simplified chain termination steps.

2.2 Metallocene Catalysts

2.2.1 The Metallocene

The main component of homogeneous catalyst systems, the catalyst precursor, is the Group 4B transition metallocenes (titanocenes, zirconocenes and hafnocenes), which are characterized by two bulky cyclopentadienyl (Cp) or substituted cyclopentadienyl ligands (Cp'). Two simple examples of these metallocenes are shown in Figure 2.4.

These molecules have C_{2v} symmetry. The two Cp rings in the molecules are not parallel. The Cp_2M fragment is bent back with the centroid-metal-centroid angle θ about 140° due to an interaction with the other two σ bonding ligands.[8]

(a) by β-elimination with H-transfer to monomer

(b) by hydrogenation

(c) by β-elimination forming hydride
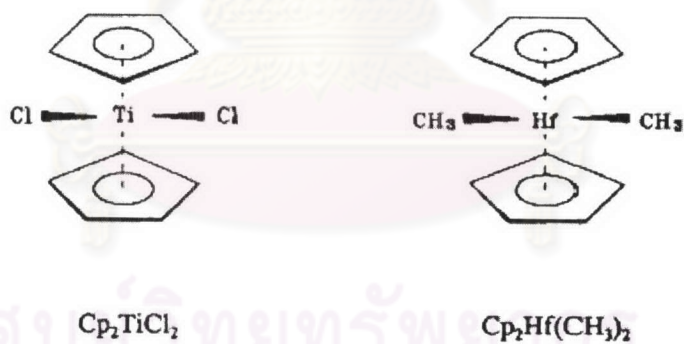

Figure 2.3 Chain termination reactions [2]

Cp$_2$TiCl$_2$ Cp$_2$Hf(CH$_3$)$_2$

Figure 2.4 Structures of two metallocenes with C_{2v} symmetry

The chiral ansa-metallocenes, that is, metallocenes with two Cp' ligands arranged in a chiral array and connected together with chemical bonds by a bridging group, were first synthesized by Brintzinger and coworkers.[9] The molecular structures of the two famous Brintzinger catalysts, Et(Ind)$_2$ZrCl$_2$ and Et(H$_4$Ind)$_2$ZrCl$_2$, are depicted in Figure 2.5.

These two metallocenes have C_2 symmetry. An ansa-metallocene can have C_2, C_s or C_1 symmetry depending upon the substituents on the two Cp' rings and the structure of the bridging unit. A large number of ansa-metallocenes have been synthesized by changing the transition metals (Ti, Zr or Hf) and substituents on the Cp rings, as well as the bridging groups. There are a wide variety of substituted Cp ligands. Among them methylcyclopentadienyl (MeCp), pentamethylcyclopentadienyl (Me_5Cp), indenyl (Ind), tetrahydroindenyl (H_4Ind) and fluorenyl (Flu) ligands are most frequently used. The common bridging groups are ethylene (Et, $-CH_2CH_2-$), dimethylsilylene (Me_2Si, $(CH_3)_2Si=$), isopropylidene (iPr, $(CH_3)_2C=$), and ethylidene ($CH_3CH=$). The bridging group not only provides a stereorigid conformation for the complex, but also dictates the distance between the transition metal atom and the Cp ligands and the bending angle θ, thus influencing catalyst activity and stereospecificity.

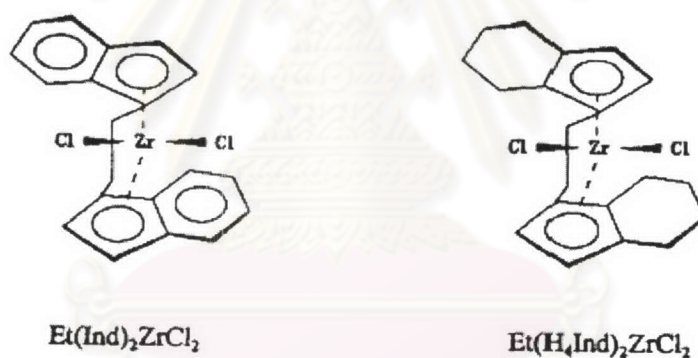$Et(Ind)_2ZrCl_2$ $Et(H_4Ind)_2ZrCl_2$

Figure 2.5 Structures of the Brintzinger catalysts [9]

It is believed that a steric interaction of the Cp type ligands surrounding the active center with incoming monomer plays a key role in the stereoselectivity of the polymerizations with these homogeneous catalysts. Changing the steric structure of the ligands in the metallocenes leads to the changes in steric structures of polyolefin products. Poly(α-olefins) of any steric structure (isotactic, syndiotactic and atactic) can be obtained simply by tailoring the stereorigid metallocene (catalyst precursor), basically according to the local symmetry.

2.2.2 The Methylalumoxanes (MAO)

MAO is the most important cocatalyst which activates the group 4B metallocenes in homogeneous Ziegler-Natta polymerization. Before the discovery of the MAO cocatalyst, the homogeneous Ziegler-Natta catalyst Cp_2TiCl_2 was activated with alkylaluminum chloride which led to poor catalyst activity. The use of MAO cocatalyst raised the catalyst activity by several orders of magnitude. There are some other alumoxanes which can also activate the metallocenes, such as ethylalumoxane (EAO) and isobutylalumoxane (iBAO), but MAO is much more effective than its ethyl and isobutyl analogous and is most preferred in practice.[10]

MAO is formed by hydrolysis trimethylaluminum (TMA). The controlled hydrolysis of TMA was first performed by the reaction of TMA with crystal water of $CuSO_4.5H_2O$. Later, $Al_2(SO_4)_3$ hydrates were chosen as the water source for the reaction, in order to prevent the contamination of MAO from Cu(I) alkyl compounds.[11,12] In recent years, some patents claimed that MAO could be made through the reaction of TMA with dimethyltin-oxide (Me_2SnO).[13]

MAO is an oligomer with 6-20 [-O-Al(Me)-] repeat units. A higher degree of oligomerization of MAO provides a beneficial effect to the catalyst activity. The exact structure of MAO remains a puzzle. Earlier research suggested that MAO might exist in a linear and/or a cyclic form.

However, based on ^{27}Al NMR spectroscopic studies, some researchers recently indicated that there appears to be no logical structure for MAO with $n > 4$, in which all aluminum atoms *simultaneously* achieve a coordination number of 4. A possible structure is shown below as proposed by Sugan Fo *et al.*[14] The presence of some three-coordinate aluminum sites is to be expected and their Lewis acidity will be enhanced by the electronegative effect of adjacent oxygen atoms (see Figure 2.6) [15].
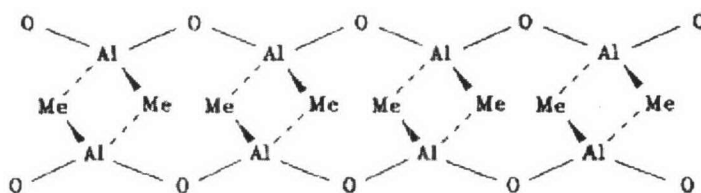
Figure 2.6 A proposed structure of MAO with a coordination number of 4 [15]

Recent studies reveal that the true active species in metallocene/MAO systems are cationic metallocene alkyls, which are d^0 14-electron complexes. The formation of the catalytically active complex involves a series of reactions between metallocenes and MAO. For the halogen-containing metallocenes, a rapid alkylation of metallocene by MAO takes place first, and the active species arises from a methyl transfer reaction between the metallocene alkyls and MAO. The active species formed from these reactions is probably in combination with a poorly coordinating MAO anion.

2.3 Microstructure of Propylene

2.3.1 Bridged metallocene with rac-C$_2$-symmetry

2.3.1.1 Catalysts and polymerization mechanism.

The modification of Cp$_2$MtX$_2$ complexes aimed at the development of highly enantioselective polymerization catalysts has been carried out in several ways. The most obvious and - to now - also the most successful strategy towards isotactic-selective catalysts is a substitution of the Cp rings resulting in a chiral, C$_2$-symmetric coordination environment of the transition metal. Typical precursors can be described in terms of the two structural types (**I**) and (**II**), with suitable substituents on the aromatic ligands (and usually with Mt=Zr).

The bridge connecting the two Cp rings prevents their rotation and locks them in a chiral configuration. In most cases, -X- is -Me$_2$Si-, -Me$_2$C- or -CH$_2$CH$_2$-,

although a number of other examples have been reported [16,17,18]. For type (**I**), highly enantioselective catalysts can be obtained when (preferably bulky) substituents are present at positions 3,3' or 4,4'. In type (**II**), the role of such substituents is played by the benzene rings of the 1-indenyl moieties, although additional substitution, particularly at positions 4,4', is highly beneficial. In all cases, ancillary substituents at positions 2,2' result in a higher average molecular mass of the polymers produced.

The stereoselectivity of catalysts derived from such complexes is well understood, and detailed molecular mechanics calculations have been reported [8] for models of the active species, like the one shown in Figure 2.7 for a simple representative of type (**II**), i.e. *rac*-Me$_2$C(1-Ind)$_2$ZrCl$_2$. The catalytic complex is pseudo-tetrahedral and cationic, with an *iso*-butyl group simulating the growing polymer chain and a propene molecule at the remaining coordination site. The aromatic ligand is in the (*R,R*) configuration; other possibilities (not shown) are the mirror (*S,S*) configuration, and the non-chiral, C_s-symmetric (*R,S*) configuration. Real catalyst precursors are usually racemic mixtures of (*R,R*) and (*S,S*) species (*rac*-complex), and should be free of the (*R,S*) species (*meso*-complex) which is non-enantioselective.

As is apparent from the model, the growing polymer chain must adopt a conformation that minimizes the steric insertion with one of the two C_6 rings of the bis-indenyl moiety. The first C-C bond, in particular, is bent to one side, and this in turn strongly favors the 1,2 insertion of propene with the enantioface that brings the methyl substituent *anti* to the said C-C bond (*re*-face for the (*R,R*)-catalytic complex, *si*-face for the enantiomorphous (*S,S*)-complex). 2,1 insertion, on the other hand, is always difficult due to direct steric interactions of the CH$_3$ group with the aromatic rings.

At the completion of each insertion step, the principle of the least-nuclear-motions suggests that the growing chain will reside at the coordination site previously occupied by the monomer (*chain-migratory* insertion mechanism [16,17]). If that is actually the case or not is immaterial for the stereoselectivity of this specific catalyst class, because the C_2 symmetry ensures the equivalence of the two active sites, which are *homotopic* (i.e. prefer the same monomer enantioface). As

a result, chain propagation is expected to be isotactic and site-controlled, with occasional …*mmmmrrmmmm...* stereo defects.
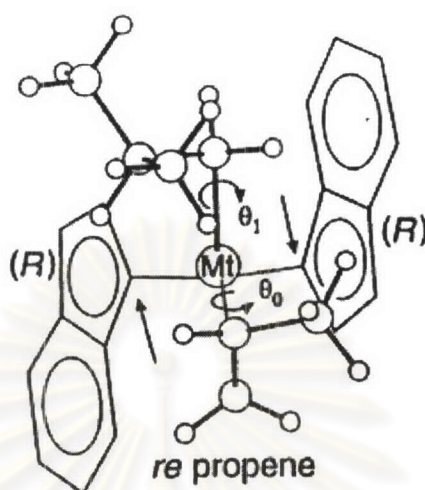

Figure 2.7 Model of a (R,R)-Me$_2$C(1-Ind)$_2$Mt(iso-Butyl)$^+$ cation (Mt = Zr), with a *re* h^2-coordinated propene molecule.[19]

2.3.1.2 Polymer configuration.

The 100 MHz ^{13}C NMR spectrum of an isotactic polypropylene sample prepared with the catalyst system rac-Me$_2$Si(1-Ind)$_2$ZrCl$_2$/MAO at T= 80°C, [C$_3$H$_6$] = 5.7 mol/l is shown in Figure 2.8. The methyl resonance is simple, with a strong peak corresponding to the *mmmm* pentad, and much weaker ones arising from the *mmmr, mmrr* and *mrrm* pentads in roughly 2:2:1 integral ratio, in agreement with the hypothesis of isotactic propagation under enantiomorphic-site control. Additional small peaks are due to regioirregular sequences (see following sub-section). The pentad distribution (Table 2.1) can be reproduced in terms of the enantiomorphic-site model [20], and the conditional probability σ in the stochastic matrix MES has a best-fit value of 0.97.

The 150 MHz ^{13}C NMR spectrum of a second polypropylene sample, obtained with the same catalyst system and at the same temperature (80 °C) but at a much lower monomer concentration ([C$_3$H$_6$] = 0.08 mol/l), is shown in Figure 2.9. It is easy to realize that the polymer is much less stereoregular than that of Figure 2.8;

as a matter of fact, the experimental stereosequence distribution is still in reasonable agreement with the enantiomorphic-site model (see again Table 2.1), but the best-fit value of the σ parameter is as low as 0.845.

This puzzling dependence of the stereoregularity on monomer concentration is unexpected on the basis of the chain propagation mechanism. The existence of a general trend of decreasing stereoselectivity with decreasing [C_3H_6] for the C_2-symmetric metallocene catalysts was noted by Busico and Cipullo [21], who proposed that it results from an intramolecular reaction of epimerization of the growing polymer chain, which competes with the polymerization. This explanation was validated by Leclerc and Brintzinger [22], who found that a significant fraction of the stereoirregular units in samples of poly(propene-l-d) made with a number of C_2-symmetric zirconocenes contain D in the *methyl* group, as a result of an isomerization process. Although the mechanistic aspects are not yet completely clarified, considerable experimental [23-25] and theoretical [26] evidence has been accumulated in favor of the epimerization pathway shown in Scheme 1.

In Figure 2.10, the dependence of the stereoselectivity of rac-Me$_2$Si(1-Ind)$_2$ZrCl$_2$/MAO on propene concentration in the whole range from infinite dilution in toluene to liquid monomer at 80 °C is compared with that of the substituted homologue *rac*-Me$_2$Si(2-Me-4-Ph-l- Ind)$_2$ZrCl$_2$/MAO. Although the two curves are qualitatively similar, it can be seen that the competing effect of chain epimerization is much less important for the latter catalyst, which is more efficient with respect to chain propagation.

Not unexpectedly, the temperature has a major effect on the stereoselectivity. Increasing the temperature favors (in relative sense) chain epimerization over monomer insertion [24], and results in a decrease of enantioselectivity of the latter process (particularly for *ansa*-metallocenes of lower stereorigidity, as are those with the conformationally flexible -CH$_2$CH$_2$- bridge) [16,17].

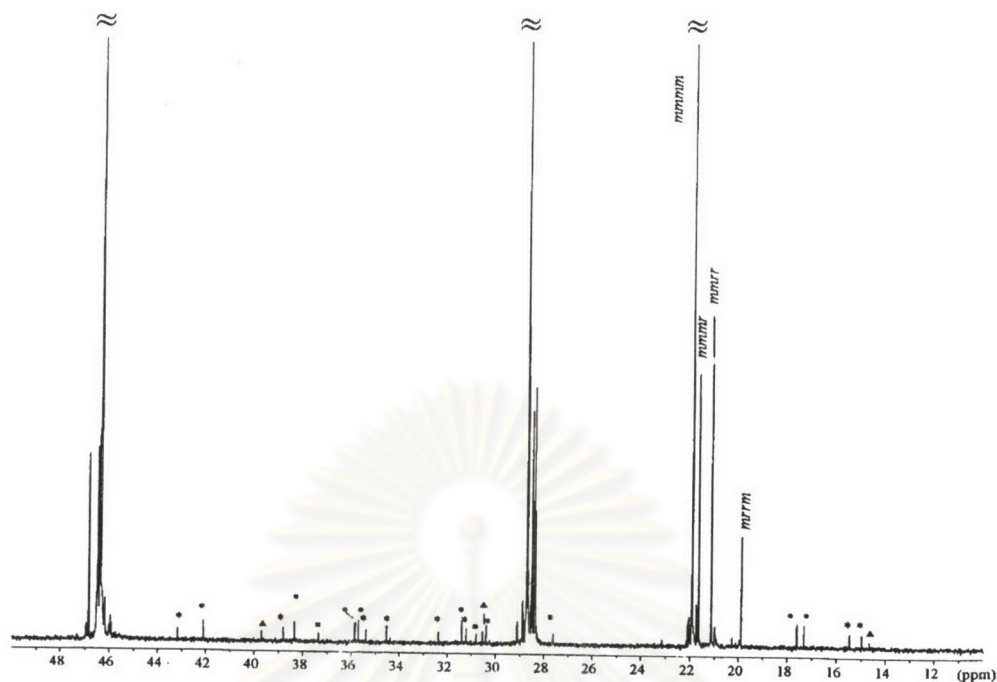**Figure 2.8** 100 MHz ^{13}C NMR spectrum of an isotactic polypropylene sample prepared with the catalyst system rac-Me$_2$Si(1-Ind)$_2$ZrCl$_2$/MAO at T= 80°C, [C$_3$H$_6$] = 5.7 mol/l (in toluene). In the methyl region, the resonances of the four main pentads in regioregular sequences are explicitly assigned. Minor peaks arising from stereoregular (●) and stereoirregular (*) isolated 2,1 units, 3,1 units (■) and propyl end-groups (▲) are also indicated.

Table 2.1 Steric pentad distributions evaluated from the two ^{13}C NMR spectra of Figures. 2.8 and 2.9, along with best-fit calculated ones in terms of the enantiomorphic-site model

Pentad	[C$_3$H$_6$] = 5.7 M		[C$_3$H$_6$] = 0.08 M	
	Fraction (exp.) (%)	Fraction (calc.)[a] (%)	Fraction (exp.) (%)	Fraction (calc.)[a] (%)
mmmm	86.6	86.5	43.2	43.1
mmmr	5.3	5.1	14.8	15.9
rmmr	[b]	0.1	2.1	1.7
mmrr	5.4	5.1	15.1	15.9
mmrm + rmrr	[b]	0.3	7.6	6.8
rmrm	[b]	0.2	2.8	3.4
rrrr	[b]	0.1	1.7	1.7
rrrm	[b]	0.2	4.1	3.4
mrrm	2.7	2.55	8.6	8.0
		$\sigma = 0.971$		$\sigma = 0.845$

[a] According to the enantiomorphic-site statistical model.

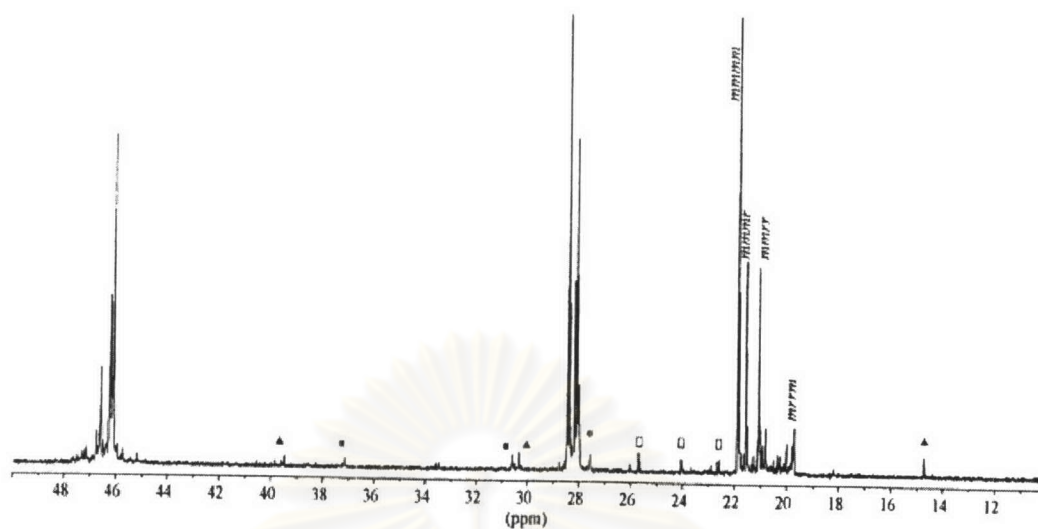[b] Too weak for accurate integration.

Figure 2.9 150 MHz ^{13}C NMR spectrum (recorded in tetrachloroethane-1,2-d$_2$ at 70°C; chemical shift scale in ppm downfield of TMS) of a predominantly isotactic polypropylene sample prepared with the catalyst system rac-Me$_2$Si(1-Ind)$_2$ZrCl$_2$/MAO at T = 80°C, [C$_3$H$_6$] = 0.08 mol/l (in toluene). In the methyl region, the resonances of the four main pentads in regioregular sequences are explicitly assigned. Minor peaks arising from 3,1 units (■), and from propyl (▲) and *iso*-butyl (□) end-groups, are also indicated.
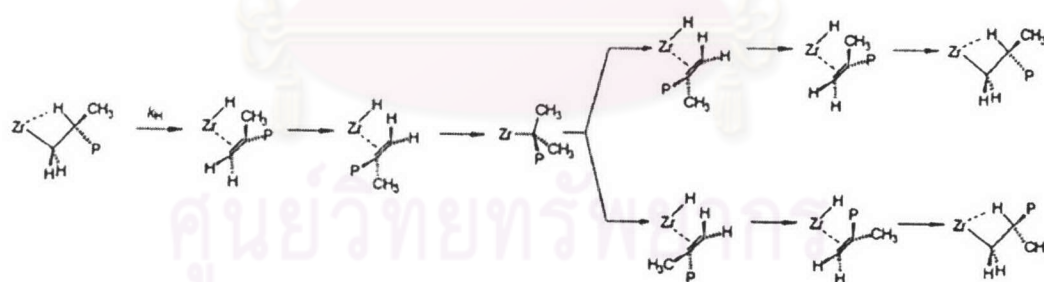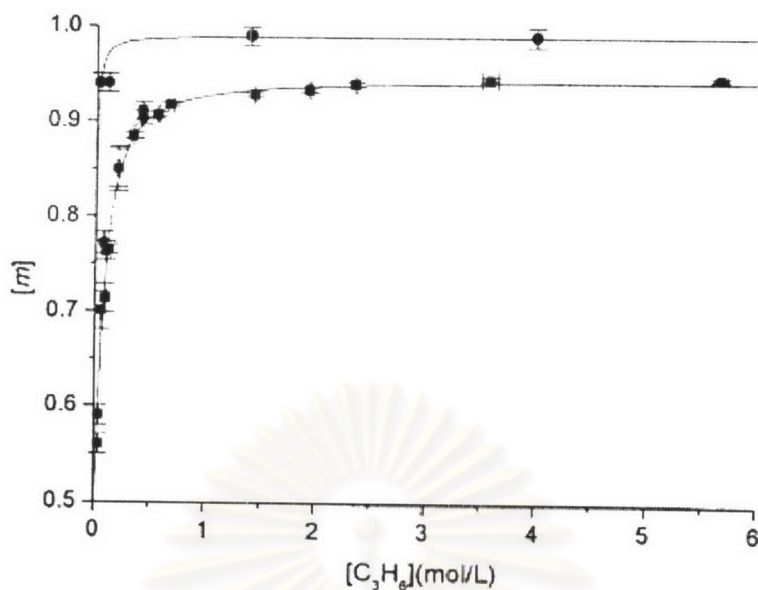

Scheme 1

Figure 2.10. ^{13}C NMR fraction of *meso* diads, [*m*] for polypropylene samples prepared at 80°C in the presence of the catalyst systems rac-Me$_2$Si(1-Ind)$_2$ZrCI$_2$/MAO (■) and rac-Me$_2$Si(2-Me-4-Ph-1-Ind)$_2$ZrCI$_2$/MAO (●), as a function of propene concentration in toluene, [C$_3$H$_6$].

In view of all this, reporting a value of stereoselectivity for a given C$_2$-symmetric metallocene without specifying the polymerization conditions makes little sense. Indeed, in all cases the lower limit at infinite monomer dilution is nil (atactic polymer); the higher limit, on the other hand, which in some cases is not reached even in liquid propene, coincides with the enantioselectivity in monomer insertion.

Importantly, irrespective of the origin (wrong enantioselection or isomerization), the distribution of the stereoerrors in the polymer chains is always Bernoullian and in accordance with the enantiomorphic site model. This is a classical demonstration that, as noted long ago by Price [27], "Markovian mathematics is only a framework within which it is possible to describe polymer chains having particular sequential characteristics, regardless of how these chains were produced".

A number of C$_2$-symmetric metallocenes with remarkably high stereo- and enantioselectivities at practical polymerization temperatures (T ≥ 70 °C) have been disclosed in recent years. Polypropylenes with [mmmm] > 0.95 (conditional probability σ > 0.99 in matrix M$_{ES}$) and melting temperature T$_m$ > 150 °C can be

obtained with catalysts belonging to both structural types (**I**) and (**II**, e.g.: *rac*-Me$_2$Si(2-Me-4-t-Bu-Cp)$_2$ZrCl$_2$ [28], rac-Me$_2$Si(3-t-Bu-Cp)$_2$ZrCl$_2$ [29], *rac*-Me$_2$Si(2-Me-4-Ph-l-Ind)$_2$ZrCl$_2$ [30], *rac*-H$_2$C(3-t-Bu-l-Ind)$_2$ZrCl$_2$ [31] (Bu = Butyl).

Also interesting for applications are 'softer', lower-melting polypropylenes with [mmmm] in the range 0.80-0.90, that can be obtained with high productivity in the presence of specific metallocenes formally deriving from structural type (II), with a further benzene ring fused in position [*e*] of the indenyl moiety (e.g. *rac*-Me$_2$Si(2-Me-Benz-[e]-1-Ind)$_2$ZrCl$_2$ [32]).

2.3.1.3 Chain constitution

On average, C$_2$-symmetric metallocenes are not exceedingly regioselective in propene polymerization. Most polypropylene samples prepared with such catalysts have a content of regioirregular enchainments in the range of 0.3-1.0 mol%; however, the regioselectivity is extremely sensitive to even small changes in the ligand framework [16,17]. Just as an indication of two extremes, polypropylenes with up to 20 mol% of regioerrors can be obtained, e.g. with rac-C$_2$H$_4$(2,4-Me$_2$-4,5,6,7-H$_4$-1-Ind)$_2$ZrCl$_2$ [33], whereas *rac*-H$_2$C(3-t-Bu-1-Ind)$_2$ZrCl$_2$ is one of the few catalysts for which the propene/ethene-[1-^{13}C] method failed to detect regioirregular propene enchainments (which suggests that these are below 0.002 mol%).
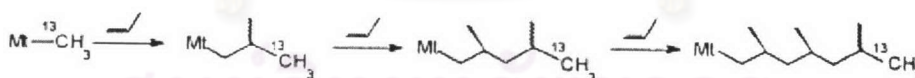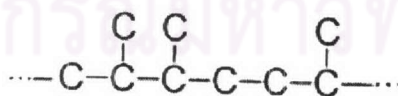

Scheme 2

Chart 2

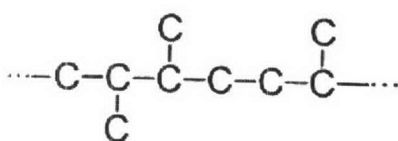Chart 3

^{13}C NMR end-group analysis proved that the predominant monomer insertion mode is 1,2. In particular, the first insertion into a Mt-^{13}CH$_3$ bond gives rise to a – CH$_2$CH(CH$_3$)-^{13}CH$_3$ end-group; it is interesting to note that this insertion is not enantioselective (Scheme 2), which confirms the crucial importance of the first C-C bond of the growing chain for the onset of the stereocontrol [34-37].

The occasional 2,1 propene misinsertions tend to remain isolated. ^{13}C NMR gave evidence for the two head-to-head enchainments shown in Chart 2 and 3 [38-39]. This indicates that: (i) 2,1 insertion is highly enantioselective (though the preferred enantioface is opposite to that favored for 1,2 insertion); (ii) the subsequent regioregular insertion occurs with lower enantioselectivity, and in some cases (e.g. metallocenes with a rather open steric environment of the transition metal, such as rac-C$_2$H$_4$(1-Ind)$_2$ZrCl$_2$ and rac-Me$_2$Si(1-Ind)$_2$ZrCl$_2$), appreciable amounts of the stereoirregular structure shown in Chart 3 are also formed.

A growing polypropylene chain with a last-inserted 2,1 unit is sterically hindered, and undergoes monomer insertion at a specific rate (k_{sp}) which, for the most crowded C$_2$-symmetric metallocene catalysts, can be up to 103 times lower than the 'normal' specific rate k_{pp} [38,41]. Therefore it can happen that, alternatively to chain propagation, this 'dormant' species isomerizes to a much less congested structure in which the last-inserted unit has a 3,1 enchainment (Chart 4) [38,42]. The commonly accepted mechanism for this isomerization, very similar to that proposed for chain epimerization (Scheme 1), is shown in Scheme 3 [42].
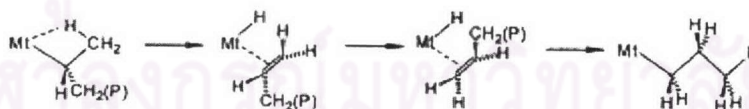
Scheme 3

In general, the total amount of 2,1 and 3,1 units in polypropylene samples produced with a given C$_2$ symmetric metallocene at a given temperature is constant, but the relative amount of 3,1 units increases with decreasing monomer concentration, because this obviously favors the intramolecular rearrangement (as already noted for the competition between monomer insertion and chain

epimerization) [38]. The trend is apparent on inspection of the two NMR spectra of Figures 2.8 and 2.9.

Increasing the polymerization temperature effects the regioselectivity both in absolute sense (increase of total regioerror content) and in relative sense (increase of 3,1 over 2,1 enchainments) [17,38].

2.3.1.4 Structure of the end-groups

Polypropylene samples produced with typical C_2-symmetric metallocene catalysts have mainly propyl and 2-methyl-prop-l-enyl (vinylidene) chain end-groups. Elegant kinetic studies [32] proved that chain transfer by intramolecular β-H elimination (Scheme 4a) is much slower than that assisted by the monomer (Scheme 4b), and that the latter can be effectively inhibited by ligand substitution at positions 2,2' (e.g. with methyl groups), which shields the catalytic complex in its equatorial belt. As a matter of fact, this substitution easily results in a 10-fold increase of polymer average molecular mass [16,17].

Additional saturated end-groups that have been observed by ^{13}C NMR [17] are *iso*-butyls, which can be traced to chain transfer with $AlMe_3$ in equilibrium with MAO (when used; Scheme 4c). ^{1}H NMR, on the other hand, may reveal low amounts of butyl-2-enyls (vinylenes), most probably arising from (monomer-assisted) β-H elimination at a last-inserted 2,1 unit (Scheme 4d) and - more surprisingly-prop-l-enyls (vinyls). It is not clear yet whether the latter are formed via β-methyl elimination (Scheme 4e) and/or allylic activation.

In the presence of H_2 (which is a well-known molecular weight regulator in coordination polymerization catalysis), the chain ends that are formed can also be apparently non-trivial. Indeed, in addition to propyl and *iso*-butyl groups, expected for a polymerization process with high 1,2 regioselectivity (Scheme 5 a and c), butyl [41,43] and - in some cases - 2,3-dimethyl-butyl ends are also observed. The former, however, are easily understood if one considers that H_2, similarly to ethene, is much faster to react with a 'dormant' site than propene (Scheme 5b) [41,43]. 2,3-dimethyl-

butyl end groups, in turn, are a clear indication that propene insertion into an initial Mt-H bond is not highly regioselective (Scheme 5d) (in accordance with the outcome of recent mixed quantum-mechanics/ molecular mechanics investigations) [44].
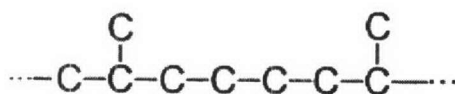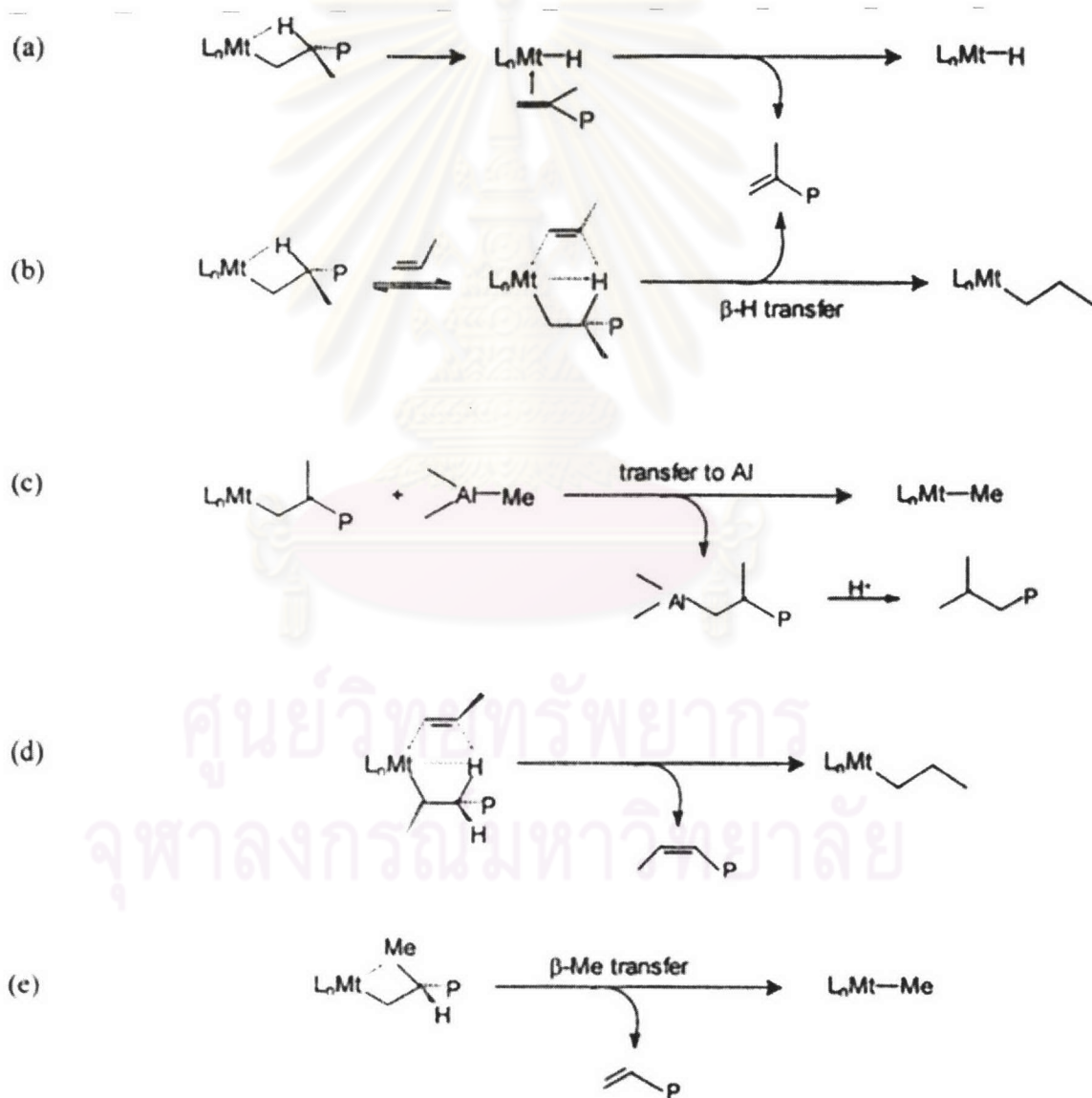

Chart 4

Scheme 4.

2.3.2 TiCl$_3$ and MgCl$_2$/TiCl$_4$-based systems

2.3.2.1 Catalysts and polymerization mechanism.

The 25 Mt of isotactic polypropylene consumed in the world in 1999 were practically all produced with technologies relying on heterogeneous catalysts that are a direct derivation of those discovered in the laboratories of Karl Ziegler and Giulio Natta in 1953-54.

The first generations of these catalysts were based on TiCl$_3$ in one of its 'violet' modifications with layered structure (α, γ, δ), in combination with an alkyl-Al-halide (e.g. AlEt$_2$Cl) [45]. Cossee was the first to suggest that the active sites are located on the thin, coordinatively unsaturated side faces of the platelet-like TiCl$_3$ crystals, and to relate the chirality of the surface Ti atoms with the stereoselectivity [46]. With some adaptations, his mechanism of isotactic chain propagation (Figure 2.11) is still considered a sound basis for the description of the polymerization process; its key points can be summarized as follows [46,47].
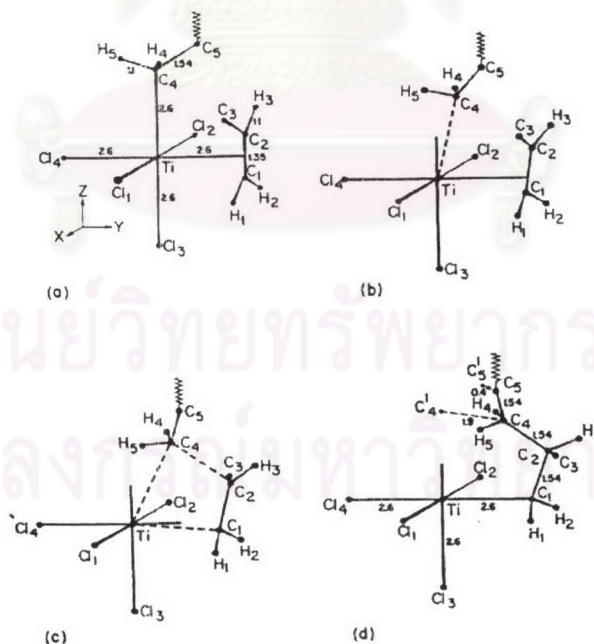

Figure 2.11 Possible propene insertion path for Ti-based Ziegler-Natta catalysts, according to Cossee [46]

(i) The Ti atoms in the bulk of 'violet' TiCl$_3$ crystals are chiral; indeed, each of them is bonded to three neighboring ones by double Cl bridges, which results in an

octahedral tris-chelate coordination with Δ or Λ configuration (Figure 2.12-top).

(ii) Plausible lateral terminations of the structural layers are obtained by breaking one out of three double bridges around the Ti atoms on the cut (e.g. parallel to the (110) or (100) crystallographic directions; Figure 2.12-bottom). This generates linear racemic arrays of enantiomorphous Ti centres with two *cis* double Cl bridges directed towards the crystal interior, and one unbridged Cl ligand (as a remnant of the third broken bridge) to ensure the electroneutrality.

(iii) The catalytic species are formed by ligand exchange with the alkyl-Al cocatalyst, which replaces the unbridged Cl with an R group. The monomer can coordinate to the remaining empty site of the octahedron, and insert into the Ti-R bond.

(iv) Monomer insertion is enantioselective due to site control, and opposite monomer enantiofaces are preferred at Ti centers of opposite chirality.

At the time of the original formulation, point (iv) was rather weak, because the steric contacts involved in the chiral recognition were not clearly identified. However, the first ^{13}C NMR characterizations of the polymers confirmed the site-controlled origin of the isotacticity, and ultimately molecular mechanics studies on models of catalytic species pointed out the key role of the growing chain in the asymmetric induction [35,47,49].

Two such models, which refer to (100) and (110) cuts of a structural layer of 'violet' $TiCl_3$, are shown in Figure 2.13 In the former case (Figure 2.13a), a local C_2 axis relates the two coordination sites available at each surface Ti atom, which implies their equivalence. In each of them, a growing polymer chain experiences repulsive non-bonded contacts with one of the Cl atoms of the surface (dashed in the figure); as a result, the first C-C bond is conformationally constrained and chirally oriented. In turn, this favors
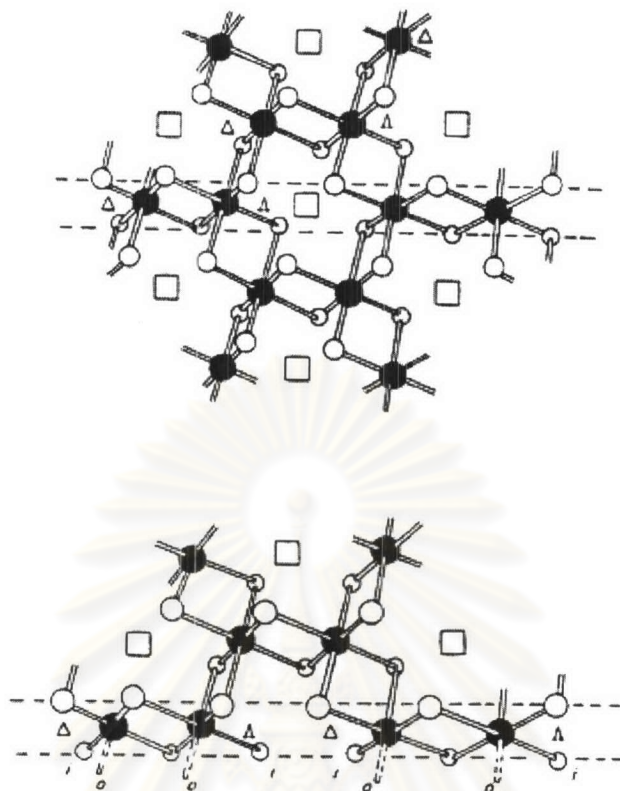
Figure 2.12 Schematic drawing of a structural layer of 'violet' TiCl₃, before (top) and after (bottom) a cut along the (110) crystallographic direction.[48].

the 1,2 insertion of a propene molecule Π-coordinated to the other site with the enantioface that brings the methyl substituent *anti* to the said C-C bond.

This mechanism of stereocontrol is strikingly analogous to that discussed for the C_2-symmetric *ansa*-metallocene catalysts (for which, of course, the role of the surface is played by the aromatic ligand framework). In both cases, a growing chain with at least one C-C bond is needed in order to pass the chiral information from the active metal to the incoming monomer, and propene insertion into a Mt-methyl bond is not enantioselective.

An analogy with C_1-symmetric metallocene catalysts can be invoked instead for the model of catalytic species on a (110) cut of TiCl₃ (Figure 2.13b). Indeed, according to molecular mechanics calculations [49], the absence of one of the two surface Cl atoms required for the orientation of the growing chain makes propene insertion at 'step $(i + 1)$' non-enantioselective. Therefore, chain propagation is

expected to be hemiisotactic if the mechanism is of chain migratory type, whereas a predominantly isotactic control can be obtained if monomer insertion occurs in preference as shown at 'step (*i*)'; recent experimental data indicate that the latter is actually the case.

In the late 1960s, 'activated' $TiCl_3$ catalysts (in some cases, containing minor amounts of $AlCl_3$ in solid solution) with specific surface areas of the order of 150 m^2/g became available [45]. These second-generation systems, that found large-scale industrial application in the 1970s and are still used today by a number of minor polypropylene manufacturers, have productivities of the order of 5 kg of polymer per g of $TiCl_3$ when used in combination with $AlEt_2Cl$; the polymers have [*mmmm*] values >0.90, DSC melting points T_m > 165°C and are almost completely insoluble in high-boiling solvents such as heptane, though minor amounts (<5% by weight) of by-products of lower stereoregularity are also formed. Higher productivities, but also (much) lower stereoselectivities, are observed when the cocatalyst is an Al-trialkyl such as, e.g. $AlEt_3$.

The main problem of the polypropylene produced with $TiCl_3$/$AlEt_2Cl$ systems is that it contains nonnegligible residual amounts of hydrolizable Cl, which requires expensive procedures of catalyst deashing. In order to increase the productivity (referred to Ti), attempts were made to support active Ti compounds (usually, $TiCl_4$) on inert matrices. Good results were obtained only with matrices structurally similar to 'violet' $TiCl_3$, such as - in particular – $MgCl_2$ [50]. The first simple $MgCl_2$/$TiCl_4$-AlR_3 systems had a productivity in excess of 10 kg of polypropylene per g of catalyst (roughly corresponding to 500 kg per g of Ti), but the 'poorly tactic' fraction exceeded 50% by weight of the raw polymer. However, spectacular increases of stereoselectivity were obtained by the addition of suitable Lewis bases to the co-catalyst (*external* donors) and/or to the solid catalyst (*internal* donors).
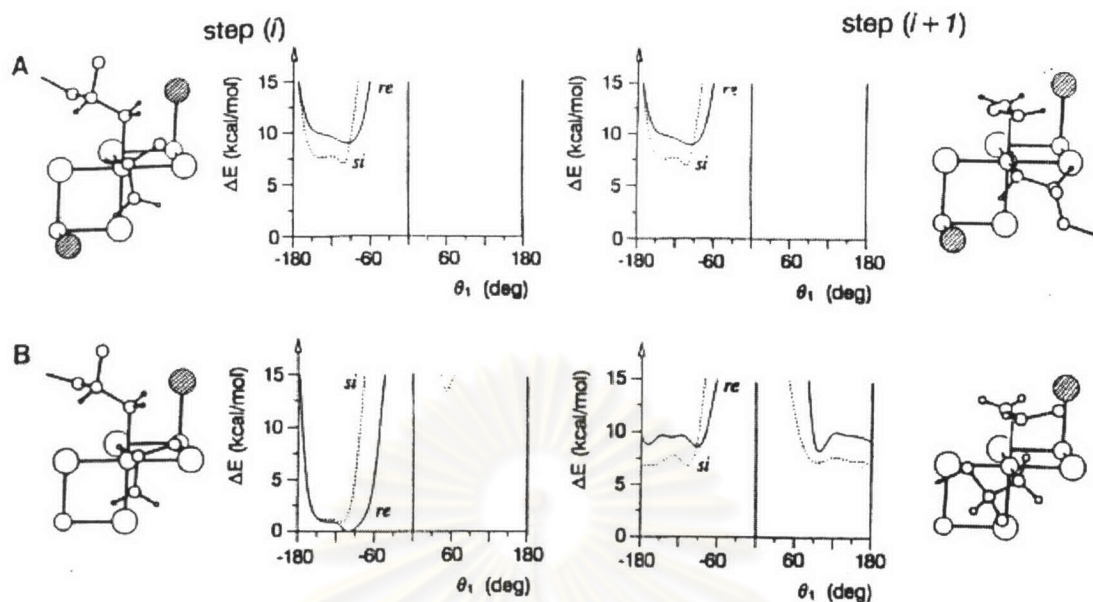
Figure 2.13 Possible models of catalytic species on a (110) (A) or (100) (B) cut of a structural layer of 'violet' $TiCl_3$. The situations labelled as step (i) and ($i + 1$) correspond to consecutive 1,2 propene pre-insertion intermediates, in the hypothesis of a chain migratory propagation mechanism. In both cases, the configuration of the active Ti centre is Δ; however, the local symmetry is C_2 for species A, C_1 for species B. According to molecular mechanics calculations (see internal energy maps shown), at the two homotopic active sites of species A propene coordination (and subsequent 1,2 insertion) is enantioselective, due to non-bonded contacts between one of the two dashed Cl ligands and the growing polymer chain, which must bend to one side. This favors, in turn, propene coordination with the *si* enantioface (shown), which orients the methyl group *anti* to the first chain C-C bond; as a result, chain propagation is predicted to be *isotactic*. On the other hand, the absence of one of the said crucial Cl ligands in the case of species B results in a loss of enantioselectivity at step ($i + 1$); this would lead to *hemiisotactic* propagation in case of a regular chain migratory mechanism (adapted from Ref. [49]).

$TiCl_4$ chemisorption takes place at coordinatively unsaturated side faces of the platelet-like $MgCl_2$ crystals. Corradini and coworkers and, more recently, Barino and Scordamaglia showed how epitactic coordination of $TiCl_4$ units to (100) and (110) cuts of $MgCl_2$ structural layers can give rise to a variety of catalytic species, some of which are practically identical to those previously proposed for 'violet' $TiCl_3$ (Figure

2.14). It seems likely that the Lewis bases used as catalyst modifiers are able to 'poison' the most 'open' of these Ti species, that would be unable to exert a strong stereocontrol on the polymerization, and/or to change them into stereoselective species by providing the necessary steric hindrance.

The last generations of MgCl$_2$-supported *high-yield* catalysts, modified with aromatic diesters or 1,3diethers as internal donors and alcoxysilanes as external donors, afford polypropylenes with [*mmmm*] values well above 0.90 and negligible contents of 'poorly tactic' by-products, with a mileage in excess of 100 kg of polymer per g of catalyst [50].
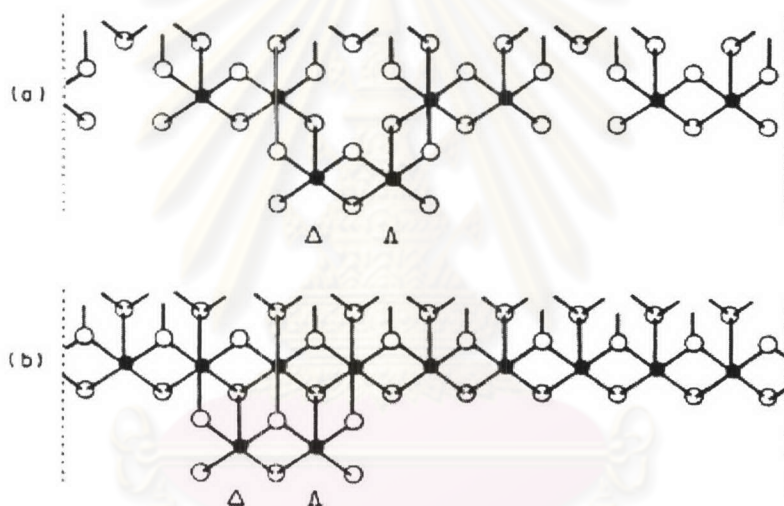
Figure 2.14 Model of a Ti$_2$Cl$_6$ relief on a (110) cut of a structural layer of 'violet' TiCl$_3$ (a), and of a Ti$_2$Cl$_6$ species chemisorbed epitactically on the (100) cut of a structural layer of MgCl$_2$ (b).

2.3.2.2 Chain configuration.

The multi-site nature of Ziegler-Natta systems (either TiCl$_3$-based or MgCl$_2$-supported) results in the fact that the polypropylenes produced are complicated mixtures of macromolecules with different tacticity (from highly isotactic to poorly isotactic (*isotactoid*) and — even — predominantly syndiotactic) [47].

A rough but practical method for evaluating the stereoregularity of a given polymer sample is to measure the weight fraction that is insoluble in a certain solvent under certain conditions, and as such is conventionally referred to as 'isotactic'. Although it is well known that polymer solubility depends on the molecular mass as well, it is commonly assumed that in the range of average molecular masses of commercial grade polypropylenes this dependence is only marginal, and that the fractionation is mainly governed by tacticity [45].

Two popular (and substantially equivalent) procedures are extraction with boiling heptane and fractional crystallization after complete dissolution in hot (>130°C) xylene. The so-called *index of isotacticity* (*II*) is the weight fraction of polymer insoluble in boiling heptane; the weight fraction of polymer which crystallizes from xylene solution at room temperature, instead, is called *xylene index* (*XI*) [45].

Polypropylene samples made with industrial catalysts are characterized by *II* and/or *XI* values higher than 95% [45]. ^{13}C NMR confirms the effectiveness of the fractionation, in the sense that typical 'isotactic' fractions (i.e. heptane- or xylene-insoluble) have values of [*mmmm*] in excess of 0.90; however, in most cases the spectra also reveal low amounts of syndiotactic blocks, owing their insolubility to the fact they are chemically bound to the isotactic part [51].

The polymer fraction soluble in boiling heptane or in xylene at room temperature, in turn, is often referred to as 'atactic', although it has long been recognized that this notation is not appropriate. Indeed, no truly atactic chains are found in such fraction, which contains instead poorly isotactic (isotactoid) and syndiotactic sequences. 'Atactic' fractions made with $MgCl_2$-supported systems have a certain stereochemical variability; in particular, the use of an 'external' donor tends to increase the relative amount of syndiotactic sequences, which in a few special cases can even become predominant [52]. Quite surprisingly, recent high-field ^{13}C NMR investigations proved the presence also of isotactic sequences, occurring in the form of short stereoblocks (which largely prevents their crystallization) [53].

The above indicates that the difference between 'isotactic' and 'atactic' fractions is less clearcut than has long been assumed, and that the mechanisms of stereocontrol leading to their formation are intimately related.

A high-field ^{13}C NMR study of a polypropylene sample obtained with the catalyst system $MgCl_2/TiCl_4$ — 2,6-dimethylpyridine/$AlEt_3$ has been recently reported [53]. This system is peculiar in that it affords polypropylenes with relatively high amounts of crystallizable syndiotactic sequences both in the 'atactic' and in the 'isotactic' fraction; therefore, in the statistical analysis of chain configuration, it can be assumed that the average length of such sequences is high enough to neglect the presence of block junctions with the isotactic part that would represent a major source of complication.

Figures 2.15 and 2.16 show the ^{13}C NMR spectra of the 'isotactic' (xylene-insoluble) fraction and of an 'atactic' (diethyl-ether-insoluble/pentane-soluble) sub-fraction, respectively. Resonance attributions are given, along with the normalized stereosequence distributions obtained by full spectral simulation. The latter could be reproduced satisfactorily only in terms of a linear combination of *three* statistical models: enantiomorphic-site, chain end, and chain migratory with diastereotopic sites. This required eight adjustable parameters: conditional probabilities σ of matrix $\mathbf{M}_{ES}$ and P_r of matrix $\mathbf{M}_{CE}$; σ_1, σ_2, P_{12}, P_{21} of matrix $\mathbf{M}_{CM\text{-}Cl}$; mixing coefficients (weight fractions) w_{ES} and w_{CE} (of course, $w_{CM\text{-}Cl} = 1 - w_{ES} - w_{CE}$).
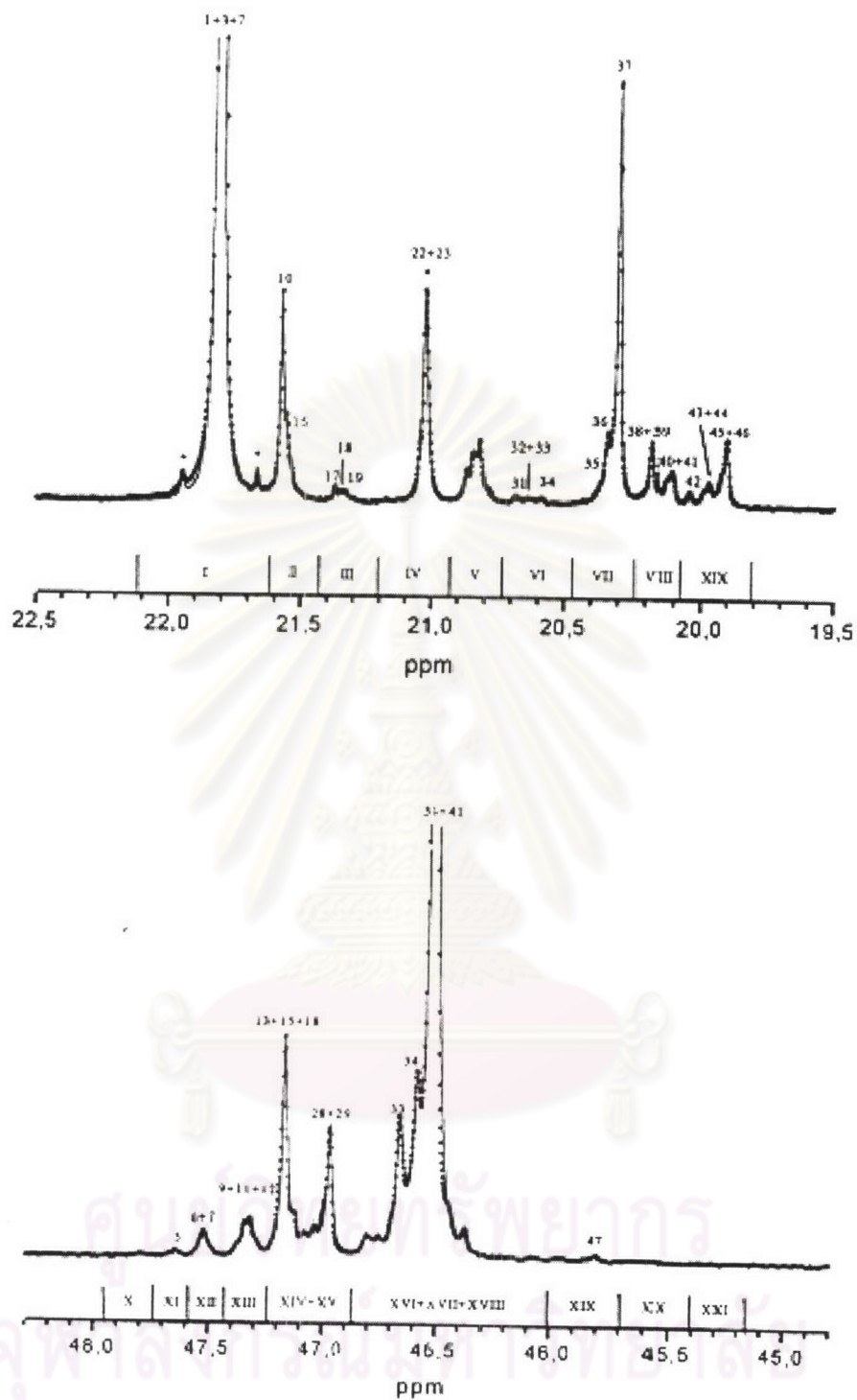
Figure 2.15 Methyl (top) and methylene (bottom) regions of the 125 MHz ^{13}C NMR spectrum of the xylene-insoluble fraction of a polypropylene sample prepared with the catalyst system MgCl$_2$/TiCl$_4$-2,6-dimethylpyridine/AlEt$_3$[54].
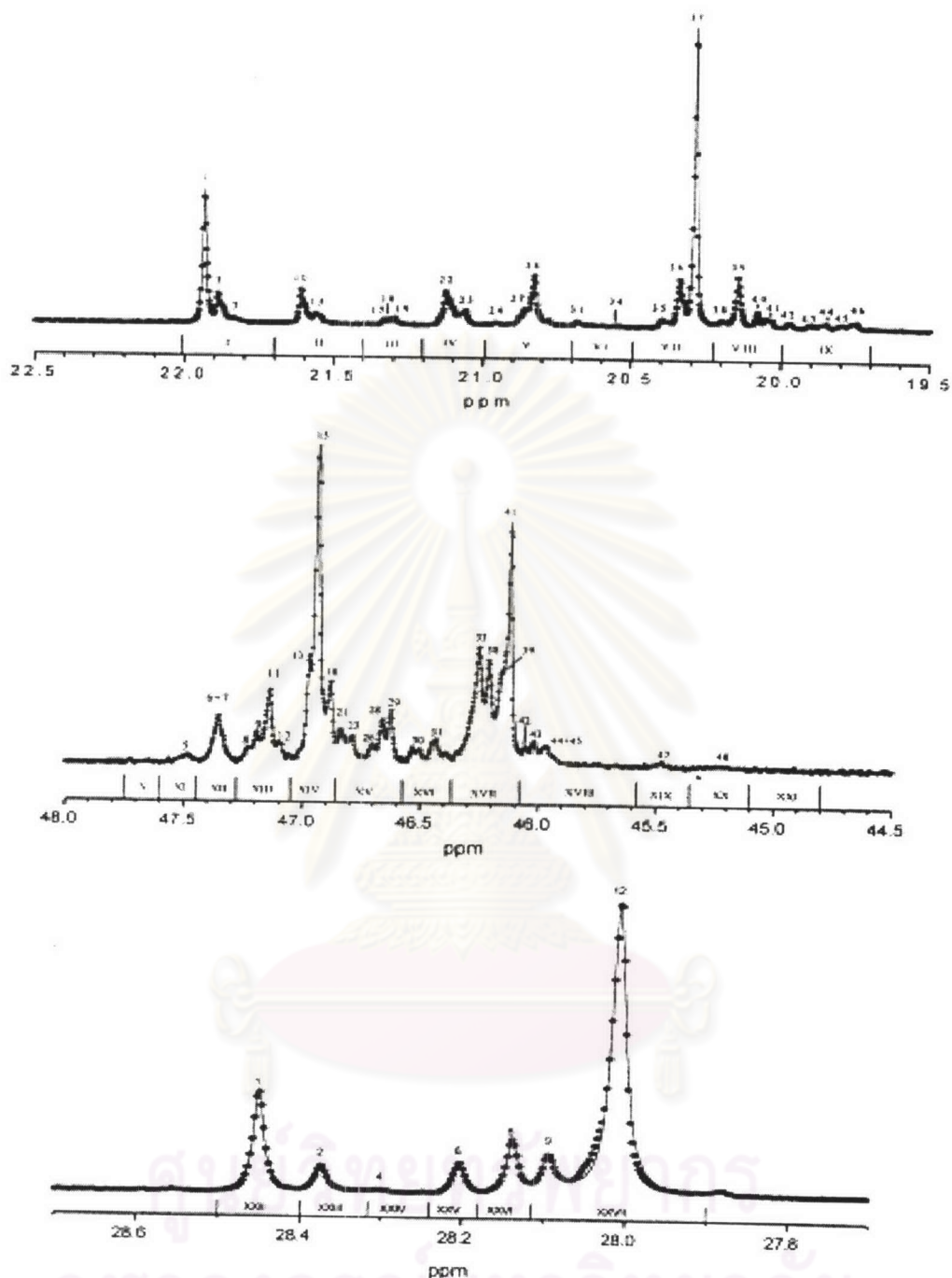
Figure 2.16 Methyl (top), methylene (centre) and methine (bottom) regions of the 150 MHz ^{13}C NMR spectrum (recorded in tetrachloroethane-1,2-d_2 at 70°C; chemical shift scale in ppm downfield of TMS) of the diethyl-ether-insoluble/pentane-soluble fraction of a polypropylene sample prepared with the catalyst system MgCl$_2$/TiCl$_4$ - 2,6-dimethylpyridine/AlEt$_3$[54].

According to this interpretation, the two fractions comprise the same three configurational 'building blocks' (Chart 5): highly isotactic (enantiomorphic-site-controlled − A); syndiotactic (chain-end-controlled −C); isotactoid (B). The latter have a configurational statistics very similar to that observed for predominantly isotactic samples obtained in the presence of C_1-symmetric ansa-metallocenes particularly revealing is the substantial absence of consecutive stereoerrors (.. .mrmr. .. sequences, Chart 6), in spite of a rather poor average stereoregularity, and the trend of increasing isotacticity with decreasing monomer concentration [55].

The main difference between the two fractions is the relative amount of the three constituting stereosequences: the xylene-soluble fraction contains predominantly isotactoid (w_{CM-Cl} = 0.43) and syndiotactic (w_{CE} = 0.47) blocks, whereas the xylene-insoluble one is made in prevalence of highly isotactic blocks (w_{ES} = 0.51).

Qualitatively, the above picture seems to have a general validity for $TiCl_3$ and $MgCl_2/TiCl_4$ catalysts, although the specific nature of the catalyst system has profound effects on the quantitative aspects of polymer configuration. For $MgCl_2$-supported catalysts, in particular, the modification with different Lewis bases may result in largely different polymerization products.

As an example, A polypropylene sample prepared with the catalyst system $MgCl_2$/di-(iso-butyl)phthalate/$TiCl_4$ - $AlEt_3$/phenyl-triethoxysilane. Also in this case, the configuration of the xylene-insoluble and xylene-soluble fractions can be described in terms of the previously discussed three-site model; however, relative to that of the $MgCl_2/TiCl_4$ − 2,6-dimethylpyridine/$AlEt_3$ system, the use of an internal donor coupled with a more effective external donor resulted in a drastic decrease in the proportion of syndiotactic and isotactoid sequences, and also in an increased stereoregularity of the latter.

This configurational description of Ziegler-Natta polypropylenes fits nicely with their physical properties [53]. In particular, it provides a simple explanation for

the fact that such polymers melt invariably at higher temperatures than those prepared with metallocene catalysts and containing the same *average* fraction of stereoirregularities indeed, it is easy to understand that a random distribution of stereodefects corresponds to a lower *average* length of perfectly isotactic sequences, compared to the case in which such stereodefects are segregated in isotactoid blocks. On the other hand, it also accounts for the (otherwise surprising) observation, in the X -ray diffraction spectra of heptane-soluble ('atactic') fractions, of weak isotactic crystallinity [53], which can be traced to the low amounts of highly isotactic blocks.
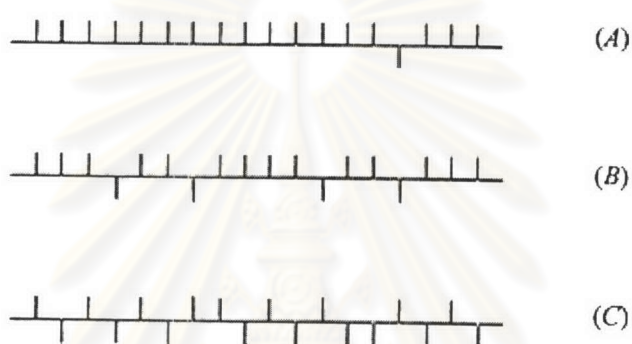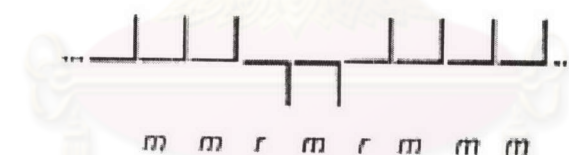

Chart 5

Chart 6

A model of catalytic species consistent with the said configurational statistics has been recently proposed (Figure 2.17) [53]. The basic structure of the catalytic complex is the chiral octahedral one proposed by Cossee. However, differences in the substitution of the two coordination positions labelled in the figure as L1 and L2, known to be crucial for the onset of site control in terms of the 'growing-chain orientation' mechanism (see also Figure 2.13), are invoked to explain the three observed types of chain propagation. In particular, this would be highly isotactic whenever (bulky) ligands (e.g. Cl atoms, Al-alkyl or Lewis base molecules) are present at both positions (with a resulting C_2 or *pseudo*-C_2 symmetry and homotopic active sites); isotactoid, when one of the two positions is vacant (C_1 symmetry and

diastereotopic sites); syndiotactic, when both positions are vacant, so that site control is lost and chain-end control can become influent. A variety of surface Ti complexes corresponding to one of these three basic structural types can be envisaged, in particular for $MgCl_2$-supported catalysts.

Ligand exchanges at the two coordination positions can result in reversible switches between the different types of stereocontrol, with the formation of stereoblock chains. 'Second-order' effects (such as the conditional probability of monomer insertion at the weakly enantioselective active site of the C_1-symmetric species, and therefore the average content of stereoirregularities in the isotactoid sequences) can be related to the specific nature of the ligand(s) involved in such equilibria, and in particular of the Lewis bases used as catalyst modifiers.

More detailed studies of polymer fractionation are unquestionably needed in order to complete the picture. Up to now, high-field ^{13}C NMR characterizations of polypropylene samples subjected to temperature rising elution fractionation (TREF) have not been reported, and only pentad data are available (which is not enough for a realistic configurational analysis). Both for 'violet' $TiCl_3$ and for $MgCl_2/TiCl_4$ catalysts, fractions of exceedingly high regioregularity ([$mmmm$] > 0.98) were isolated; it seems important to verify whether the distribution of stereodefects is not random even in such fractions.
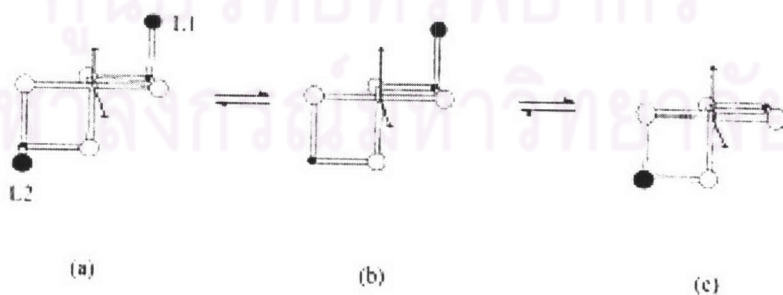

Figure 2.17 Schematic models of active species for highly isotactic (a), isotactoid (b), and syndiotactic (c) propagation in heterogeneous Ziegler-Natta catalysts (see text). (o) = Ti; (•) = Ti or Mg; (o) = Cl; (•) = Cl or donor (adapted from Ref. [53]).

2.3.2.3 Chain constitution and structure of the end-groups.

Most heterogeneous Ziegler-Natta catalysts are highly regioselective in propene insertion. The ^{13}C NMR spectra of raw polymers usually give no evidence of regioerrors, which means that their concentration is below 0.1 mol% (indicatively). Occasionally, traces of head-to-head enchainments were detected in the spectra of xylene-soluble or heptane-soluble ('atactic') fractions.

The ^{13}C NMR analysis of the end-groups formed in the presence of ^{13}C-enriched Al-alkyls proved that the predominant propene insertion mode is 1,2 [34]. This is also consistent with the ^{1}H NMR observation of 2-methyl-but-2-enyl (vinylidene) structures deriving from (monomer assisted) β-H elimination.

When H_2 is used as a chain transfer agent, mostly propyl, *iso*-butyl and butyl end-groups are detected by ^{13}C NMR [57] (Scheme 5). The amount of butyl structures often exceeds that of *iso*-butyl ones, which has been taken as an indication of a significant 'dormancy' of the growing chains due to occasional 2,1 propene misinsertions. From the fraction of butyl endgroups in H_2-terminated polymers, it is possible to estimate a lower limit for catalyst regioselectivity; values comprised between 99.8 and 99.99% can be desumed for typical $MgCl_2$-supported systems [58]. Recently, the presence of 2,3-dimethyl-butyl end-groups, particularly in polypropylene fractions of low stereoregularity, has also been documented; this indicates that propene insertion into an initial Ti-H bond is not fully regioselective (as already found for a number of *ansa*-metallocene catalysts).
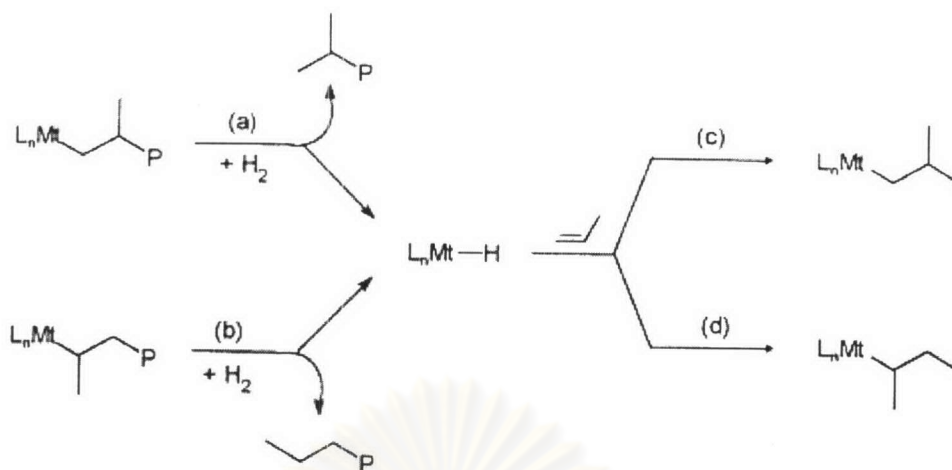
Scheme 5

2.4 Characterization of Polypropylene Tacticity by Solvent Extraction

One of the fascinating features of polypropylene is the possibility of stereoisomer formation. Thus Natta [66] distinguished three possible stereoisomeric sequences resulting from the intrinsic asymmetric nature of the tertiary carbon atom in the propylene repeating unit. Sequences of monomer units of uniform configuration were termed *isotactic*, whereas sequences of alternating configuration were known as *syndiotactic* and random arrangements were designated *atactic*.

However, it was swiftly realised that although catalysts were available which could produce predominantly isotactic or syndiotactic polymers the *as-polymerized* samples were rarely stereochemically pure and consisted of mixtures of isotactic (or, syndiotactic), stereoblock and atactic macromolecules. These fractions were initially separated by procedures based on solvent extraction and characterized on the basis of their X-Ray diffraction patterns [66]. The fundamental distinction between the different tacticities centres on their relative facility in crystallization. Thus isotactic polypropylene crystallizes readily, whereas, the atactic samples are obtained as amorphous materials.

As a consequence, effectively all of the early characterization methods were based on the measurement of parameters related to the crystallinity of the material

and only indirectly related to the actual tacticity. Such parameters include solubility. IR absorbance, density, melting point, and X-Ray diffraction. Experimental methods employing these techniques have been briefly reviewed elsewhere [67].

NMR studies of polypropylene revolutionized the determination of tacticity when it was realized that the relative steric configuration of neighboring units affected the chemical shifts of both proton and carbon atoms in the propylene repeating unit. It now became possible to quantitatively determine stereo-sequences within the polymer chain. For purpose of quantitative analysis it was necessary to introduce a nomenclature to specify two distinct arrangements known as *diads* [68]. An isotactic diad (symbol m) represented the situation where the neighboring unit has the same stereochemistry as the specified unit, whereas, a syndiotactic diad (symbol r) represents a neighboring unit of opposite configuration. Rapid developments in high field proton NMR and subsequently ^{13}C-NMR permitted the distinction of longer stereosequences as first triad, then pentad and subsequently heptad sequences became resolved. The nomenclature for these longer sequences are based on the diad definition, for example, for sequences of three repeat units. three distinct triads may be specified: isotactic (mm), syndiotactic (rr) and hetereotactic (mr) where the symbols refer to the configuration of the neighboring units relative to the specified unit. Analogous designations are used for longer sequences. These developments have been reviewed in a general way by a number of authors [69].

Elucidation of the tacticity of polypropylene samples is important from two viewpoints. Firstly, detailed structural information is increasingly becoming an important tool for understanding mechanisms of chain growth and the stereo-regulating abilities of catalyst systems. Secondly, since only the isotactic material is of commercial significance, the determination of tacticity is of crucial importance in evaluation of catalyst efficiency with respect to the formation of the isotactic product. This latter aspect is of particular relevance today, amidst the search for catalysts of ever higher activity.

Whereas, unquestionably the NMR method provides the most rigorous and fundamental evaluation of polymer tacticity yet the technique is specialized, time-consuming and requires expensive instrumentation. Consequently, secondary methods

employing relatively simple and rapid evaluation techniques are still widely used and continue to make an important contribution to propylene polymerization studies.

The differential solubility of isotactic and atactic material proved to be of inestimable importance in the initial characterization of these polymers. Natta and coworkers [70] subsequently postulated an isotactic index which was equivalent to the percentage of a given sample insoluble in boiling n-heptane. This index is still widely utilized in evaluation of PP stereoregularity. Subsequently, a more detailed correlation between isotacticity and solubility in various was published [71].

Table 2.2 Data of Natta [71] relating solvent fractionation to stereoregularity.

Insoluble in	Soluble in	% Crystallinity	MPt. °C	% Irregularity
ether	n-pentane	15-27	106-114	26.1-29.5
n-pentane	n-hexane	25-37	110-135	17.3-27.8
n-hexane	n-heptane	41-54	147-159	17.2-12.2
n-heptane	2-ethylhexane	52-64	158-170	2.5-3.4
2-ethylhexane	n-octane	60-66	174-175	0.4-0.8
n-octane	-	64-68	174-175	0.4-0.8
Trichloroethylene	-	75-85	176	0

The validity of this method was evaluated by Quynn *et al* [72] In comparison with alternative methods for determining PP crystallinity, e.g., by density and IR methods. It was shown that whereas, the IR and density methods provide a consistent measurement of crystallinity, as judged by X-Ray diffraction measurements, the heptane insolubility index was somewhat dependent on the molecular weight of the sample and did not give a reliable guide of crystallinity.

Subsequently, in seeking to refute conclusions as to the effect of the nature of the base metal-alkyl on the stereospecificity of the catalyst, Firsov *et al* [73] showed that the isotacticity index based on solvent extraction did not correlate well with IR and X-Ray measurements. In particular their work showed that the extent of

extraction was dependent on mollecular weight as well as stereospecificity.

Recently, during the course of the synthesis of low molecular weight polypropylene samples [74] we have confirmed the validity of the above criticism by comparison of the stereoregularity of samples through solvent extraction and ^{13}C-NMR measurements (Table 2.3).

Table 2.3 Comparison of polypropylene stereoregularity from ^{13}C-NMR and solvent extraction measurements.

Sample [a]	[ZnEt$_2$] [b] m mol/l	Mn$_T$ [c] × 10^{-4}	Isotactic [d] Index	(mm) [e]
5 Whole	0	30.2	71.4	0.79
HI		44.8		0.89
S		14.8		0.39
11 Whole	400	1.26	21.7	0.83
HI		11.3		1.00
S		0.84		0.77
6 Whole	600	0.91	28.0	0.87
HI		10.9		0.98
S		0.8		0.83

a) Whole sample; b)TiCl$_3$.Type 1.1/AliBu$_3$ catalyst; c) Mn as measured by tritium tracer technique; d)% insoluble in boiling n-heptane; e)triad isotacticity by NMR

It is clear from this table that for low molecular weight polymers the isotactic index as deduced by solvent extraction does not give meaningful results. Thus, whereas the isotactlcity of the samples in the presence of high concentrations of transfer agent appears to be reduced from 71% to about 30%, the NMR measurements show that in fact the overall stereoregularity of the samples increase from about 79% to 87%. This is presumably associated with the deactivation of the less stereospecific, more exposed sites by interaction with the transfer agent. Examinations of the molecular weights of the insoluble and soluble fractions show clearly that the latter are very much lower than the former and that this effect is accentuated as the overall molecular weight of the sample is reduced. It might be supposed that the molecular

weight of the atactic polymers are intrinsically lower than the isotactic fraction.

This suggestion is not unreasonable since sites producing atactic polymer are probably more open to chain transfer with metal alkyl. However, it is plain from the results cited in the table that for low molecular weight samples the soluble fraction is quite stereoregular (mm = 0.77-0.83), This clearly shows that the solubility in boiling heptane is dependent not only on stereoregularity but also on molecular weight.

Table 2.4 Comparison of solvent extraction versus NMR tacticity from the data of Martuscelli et al [75].

Sample Code	Isotactic Index		Mn $\times 10^{-4}$	Crystallinity By X-Ray (%)
	% Heptane Insoluble	^{13}C-NMR		
LY-97.5	97.5	0.956	5.5	64
HY-97.5	97.5	0.953	5.8	68
HY-96	96.0	0.949	-	68
HY-90	90.0	0.879	-	57
VHY-97.5	97.5	0.953	7.2	65

Admittedly the above data are drawn from an extreme case with low molecular weight polypropylene. A comparison of the heptane insoluble versus NMR stereospecificity taken from recent results [75] shows a better correlation (Table 2.4). In this case the isotactic index as determined by solvent extraction agrees within about 2% that determined from NMR. It is apparent therefore, that for high molecular weight highly isotactic material the solvent extraction method gives a good indication of isotacticity. This is perhaps not altogether surprising since pure isotactic polypropylene will be highly crystalline and as such not significantly soluble in boiling n-heptane which has a boiling point (98.4°C) which is lower than the melting point of the isotactic material. Thus the top point of the isotacticity index is likely to be coincident by extraction and NMR methods. However, even in the absence of molecular weight effects the two measurements are likely to diverge increasingly as the true isotacticity decreases. This follows since the solubility in n-heptane is actually a function of crystallinity and this parameter is not directly proportional to isotacticity as is discussed subsequently in this paper. It should be borne in mind too,

that the effect of hot solvent extraction is not only to remove less isotactic material but also to anneal the residue, and thus increase the crystallinity of that material.

In summary, solvent extraction 1s a useful semi-quantitative technique which is capable of ranking samples in order of isotacticity providing that the molecular weights of the samples are comparable.