

CHAPTER II

LITERATURE SURVEY

2.1 Innovations in Polyolefin Technology

The first commercial polyolefin, low density polyethylene (LDPE) with densities of 0.910 to 0.930 g/cm³ was produced in 1933, when two chemists at Imperial Chemical Industries (ICI), used very high pressures > 1000 atm and temperatures around 200°C to produce short chain and long chain branching. During the early 1950's, the Phillips activator-alkyl-free SiO₂/CrO₃ catalysts and the Standard Oil of Indiana molybdenum oxide catalysts were developed to polymerize HDPE. One year after Ziegler's discovery it was Natta and his colleagues who first introduced the concept of stereoselective 1-olefin and diene polymerization. Ziegler-Natta catalysts and Phillips catalyst brought into the rapid development of polyolefin technology and production of polyolefin materials exhibiting a broad range of properties (Boor, 1979; Mülhaupt, 1995; and Moore, 1996). Figure 2.1 shows schematically the innovations in polyolefin technology.

Transition metal catalyst for olefin polymerization was initiated both in the United States and in Europe in the early 1950s. The early transition metal catalyst resulted in three separate groups of processes: those of Standard Oil of Indiana, Phillips Petroleum, and Ziegler (Table 2.1). The early catalysts developed by Standard Oil were molybdenum oxide on γ -alumina activated before use by treatment with a reducing gas (e.g., hydrogen or carbon monoxide at > 300°C), however, the catalysts failed to get enough activities. No commercial polyethylenes made with molybdenum oxide catalysts are available today.

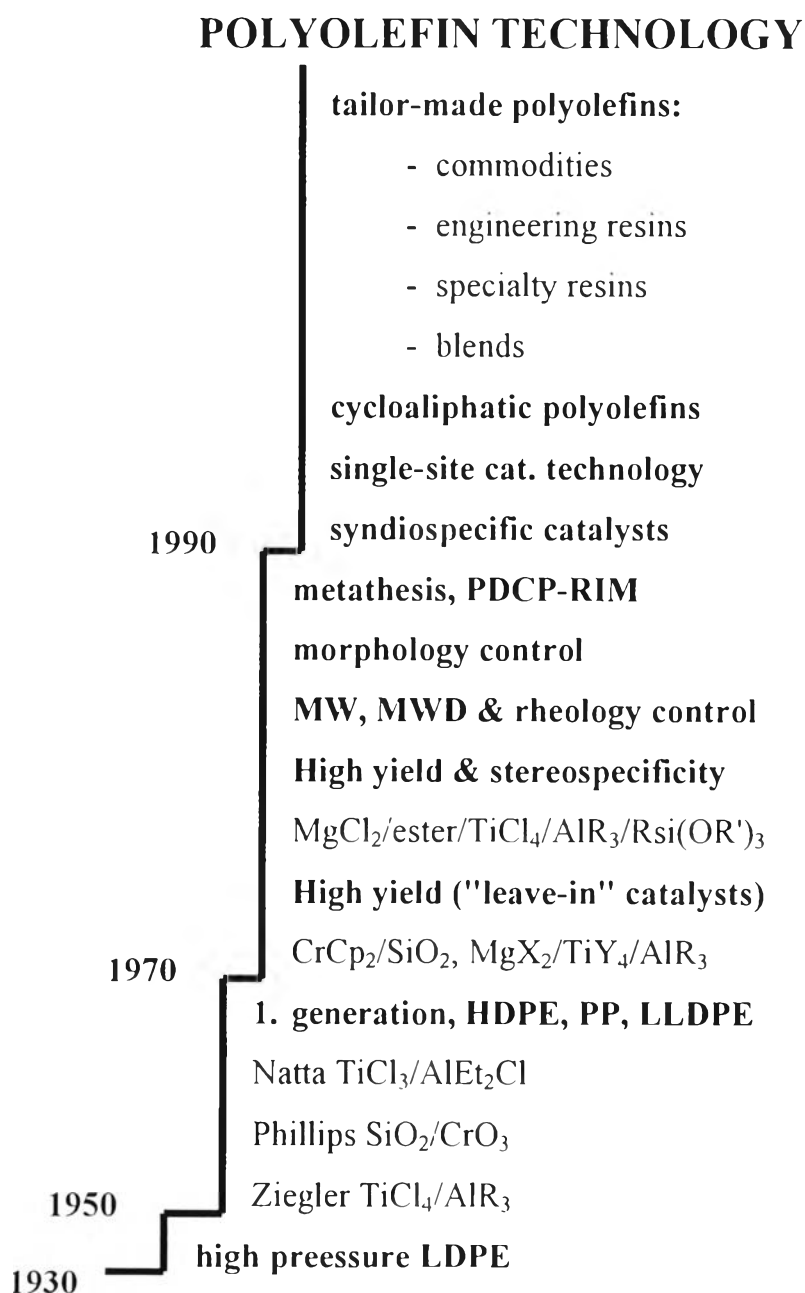


Figure 2.1 The innovations in polyolefin technology (Mülhaupt, 1995)

Table 2.1 Early discoveries of low pressure linear polyethylene (Welch and Hsieh, 1993)

Research group	Catalysts	Date	Density(g/cm ³)
Alex Zletz, Standard Oil of Indiana	Nickel oxide on activated carbon Molybdenum oxide on alumina	Early 1950	0.960
J. P. Hogan and R. L. Banks, Phillips Petroleum Co.	Chromium oxide on silica alumina	1951	0.95-0.97
Karl Ziegler et al., Max Planck Institute for Coal Research	TiCl ₄ + R ₃ Al	Late 1953	0.945

The Phillips-type catalyst discovery was chromium oxide on silica or silica-alumina support to extend catalyst life. After high temperature air activation of the catalyst and exposure to propylene, solid white material was gotten which unexpected in plug flow reactor, however, after the white solid was analyzed and found to contain a unique polypropylene, which was crystalline polypropylene. After a short time the new catalysts were used to produce high density polyethylene (HDPE) at low pressure.

In the late 1953, it was Karl Ziegler who had found that transition metal salts in combination with triethylaluminum (TEA) produced a white solid when reacted with ethylene. After that he found the most active system to be TiCl₄ reacted with TEA. In the next year Giulio Natta revealed the modified catalyst from Ziegler's discovery catalyst to form crystalline polypropylene and to extend the original discovery in new directions (Welch and Hsieh, 1993).

2.2 Magnesium Dichloride Supported Titanium Catalyst

Heterogeneous Ziegler-Natta catalysts for the syntheses of polyolefins have been considerably developed and improved through several generations of catalysts. The first-generation catalysts, based on $\text{TiCl}_3 \cdot 0.33\text{AlCl}_3$ and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, gave polypropylene (PP) containing 90 wt% of boiling heptane insoluble fractions (isotactic index, II) with a productivity of only 1 kgPP per g Cat. which were a low stereospecificity and productivity. Consequently, both removal of the catalytic residues (deashing) and separation of the atactic polymer fraction were required. To increase the fraction of accessible Ti atoms, three primary approaches were reduction of the size of the catalyst crystallites, dispersion of Ti compounds on high surface carriers, and use of soluble transition metal compounds. The second-generation catalysts, based on TiCl_3 having a much higher surface area and $\text{Al}(\text{C}_2\text{H}_5)_2\text{Cl}$, a fivefold productivity and an II around 95%, were still required removal of the catalytic residues (deashing). A drastic innovation was completed with the development of the third-generation catalysts, consisted of TiCl_4 supported on MgCl_2 by comilling with a first Lewis base (LB), usually referred to as internal donor (D_i), combined with trialkylaluminum as cocatalyst and a second Lewis base, so called external donor (D_e). These catalysts still required the atactic polymer removal that still composed from 6% to 10% of the total. The catalyst systems, which are currently used in most of the modern industrial process for PP manufacturing, was modified from third-generation catalysts to fourth-generation catalysts with a new combination of electron donors, namely alkylphthalates as D_i and alkoxysilanes (or silyl-ethers) as D_e . These catalysts can provide a superior productivity and isotacticity without any removal of the catalytic residues (deashing) and separation of the atactic polymer fraction. The fifth-generation catalysts were discovered in the second half of the 1980s with a new type of electron donors (1,3-diethers) which, if used as D_i , afforded

very high activity and isotacticity without the need of any D_e . Marvelous homogeneous metallocene catalysts, known as sixth-generation catalysts, were discovered at the same time. They can use for synthesis of almost all kinds of stereoregular and fractionally regular homopolymers and copolymers (Moore, 1996). Performance of the different catalyst generations is shown on Table 2.2.

Table 2.2 Performance of the different catalyst generations (Moore, 1996)

Gene ration	Composition	Productivity ^a (KgPP/g Cat)	I.I. (wt%)	Morphology control	Process requirements
1 st	δ -TiCl ₃ 0.33AlCl ₃ +DEAC ^c	0.8-1.2	90-94	not possible ^b	Deashing+ atic removal
2 nd	δ -TiCl ₃ +DEAC ^c	3-5 (10-15)	94-97	possible	Deashing
3 rd	TiCl ₄ /Ester/MgCl ₂ +AlR ₃ /Ester	5-10 (15-30)	90-95	possible	Atatic removal
4 th	TiCl ₄ /Diester/MgCl ₂ +TEA/Silane	10-25 (30-60)	95-99	possible	
5 th	TiCl ₄ /Diether/MgCl ₂ +TEA	25-35 (70-120)	95-99	possible	
6 th	Zirconocene+MAO	(5-9*10 ³) (on Zr) ^d	90-99 ^e	possible	

^a Polymerization:hexane slurry,70°C,0.7 Mpa,4 hrs, H₂ for MW control (values in brackets are from bulk polymerization for 2 hrs at 70°C, with H₂)

^b Only possible with Al-alkyl reduced TiCl₃, at 200-300 μ m size level

^c Diethylaluminumchloride (AlEt₂Cl)

^d One hour polymerization time

^e mmmm% (by ¹³C NMR)

Pino and Mülhaupt (1980) gave a development history of unsupported and supported catalysts. Some of the initial works on supported early transition metal catalysts are shown in Table 2.3. Even though the goal of eliminating catalyst removal process steps was not achieved, the direction was pointed and the needed encouragement to continue the efforts was provided. Table 2.4 shows a series of patents dealing with supporting halo titanium species on hydroxymagnesium halides. The work on these transition metal supported systems really began to attain fruition in the mid-1960s. A significant role in their activities was depended on the degree of dehydration of the support. To produce optimum results, the small average particle diameters and relatively high specific surface areas also helped. At the same time other groups were finding that the transition metal did not have to be pulled to the support for high activities. By the end of the 1960s, there was a great deal of interest in the new type of catalyst, which no longer required expensive removal of the catalytic residues (deashing) steps, consisting of magnesium alkoxides reacted with transition metal halides (shown in Table 2.5). All these concentrated titanium-aluminum alkyl catalyst researches gradually led to higher activity catalysts. Eventually these supported approaches brought to the catalyst systems consisting of MgCl_2 ball-milled with TiCl_4 . The results by the early 1970s were high enough catalyst activity to eliminate all deashing steps (Table 2.6) (Welch and Hsieh, 1993). The prepared catalysts by ball milling allow to grind MgCl_2 with a Lewis base and TiCl_4 together. One of the most widely used Lewis base is ethyl benzoate (EB). It is believed that EB help break down the crystalline structure of MgCl_2 . Recently, some aromatic diesters, such as dibutylphthalate, has been found that they can serve as an effective internal Lewis base in enhancing catalyst performance. Some patent examples are shown in Table 2.7. Ball milling steps can be disordered, expensive, and very energy intensive. They also tend to produce very fine polymer particles, which are difficult to handle

Table 2.3 Early supported catalysts (Welch and Hsieh, 1993)

Patent no.	Date	Company	Catalyst preparation
BP 841,822	1955	British Petrochemicals	TiCl ₄ reduced by aluminium alkyls in the presence of solids such as MgCO ₃
U.S. 3,153,634	1956	Sun Oil	TiCl ₄ was adsorbed on SiO ₂ /Al ₂ O ₃ and reduced
U.S. 2,980,662	1956	Sun Oil	Ti compounds reduced in the presence of solid NaCl, FeCl ₃ , AlCl ₃ , GaCl ₃ , etc.
BP 877,457	1957	Sun Oil	TiCl ₄ reduced in the presence of inorganic compounds

Table 2.4 Magnesium hydroxychloride supported catalysts (Welch and Hsieh, 1993)

Patent no.	Date	Company	Catalyst preparation
BP 1,024,336	1963	Solvay	Reaction of a transition metal with a hydroxychloride of a bivalent metal, preferably Mg(OH)Cl
JP45-40295	1967	Mitsui	TiCl ₄ reacted with Mg(OH) ₂ and reduced
U.S. 3,634,384	1968	B.F. Goodrich	TiCl ₄ reacted with Mg(OH) ₂ and reduced
BE 726,839	1968	Solvay	Reaction of magnesium hydroxide with a transition metal halide
BE 728,002	1968	Montecatini	
BE 735,291	1968	Hoechst	

Table 2.5 Magnesium alkoxide based catalyst (Welch and Hsieh, 1993)

Patent no.	Date	Company	Catalyst preparation
U.S. 3,644,318	1968	Hoechst	TiCl ₄ reacted with Mg(OH) ₂ or a complex magnesium alkoxide
BE 758,994	1969	Hoechst	
BE 743,325	1969	Solvay	Reaction of magnesium alkoxide and an acid halide with a tetravalent titanium compound
BE 780,530	1971	Hoechst	
NL 216,195	1971	Solvay	

Table 2.6 Magnesium chloride based catalysts (Welch and Hsieh, 1993)

Patent no.	Date	Company	Catalyst preparation
BP 1,286,867	1968	Montecatini	TiCl ₄ ball-milled with MgCl ₂ Reaction of MgCl ₂ with halogenated titanium compounds
BE 744,221	1969	Montecatini	
BE 747,846	1969	Montecatini	
JP46-34092	1968	Mitsui	TiCl ₄ reacted with MgCl ₂ • <i>n</i> ROH or MgCl ₂ • <i>n</i> H ₂ O or MgCl ₂ •Lewis base
U.S. 3,642,746	1968	Mitsui	
JP46-34093	1968	Mitsui	
BE 755,185	1969	Hoechst	Reaction of magnesium dihalide electron donor adduct (e.g., MgCl ₂ •6C ₂ H ₅ OH) with a titanium compound

in a polyolefin plant environment. Thus research on ways to make these new catalysts without the ball-milling step was continued. The ball-milled supported $MgCl_2$ catalysts have been replaced with new unsupported system. Forming these new catalysts methods consists either of precipitating dialkylmagnesium or alkylmagnesium chloride from hydrocarbon solution, or of precipitating a hydrocarbon solution of a Lewis base and magnesium dichloride. Some patent examples are shown in Table 2.8. As mentioned earlier, the ball-milling process is difficult to handle causing ongoing to attain $MgCl_2$ -rich support material from a variety of magnesium based precursors, such as Grignard reagents ($RMgX$ where R is alkyls, X is halides), magnesium dialkyls, magnesium diaryls, alkyl magnesium alkoxides, and

Table 2.7 Examples of ball milling catalysts (Yang, 1994)

Patent no.	Date	Company	Catalyst system
EP 45,977	1982	Montedison	$(MgCl_2 + \text{phthalic anhydride} + TiCl_4)_{\text{milled}}$ + $ClCH_2CH_2Cl$ -TEA + $PhSi(OEt)_3$
JP 62,181,308	1987	Toho Titanium	$(MgCl_4 + Al_2O_3 + TiCl_4 \cdot \text{dibutylphthalate})_{\text{milled}}$ + $TiCl_4$ -TEA + $Ph_2Si(OMe)_2$
JP 63,156,806	1988	Mitsubishi	$(MgCl_2 + \text{diheptylphthalate})_{\text{milled}}$ + $TiCl_4$ + heptane -TEA (prepolymerization)/ $Me_3CSiMe(OMe)_2 + AlCl_3$ -TEA
JP 63,175,006	1988	Toho Titanium	$(Mg + I_2 + BuCl) / \text{dibutylphthalate} + TiCl_4$ + $Mg \text{ stearate}$) _{milled} + $(TiCl_4 + \text{toluene})$ - (TEA + TMPIP)
JP 02,145,605	1990	Toho Titanium	$[(Mg + I_2 + BuCl) + \text{dibutylphthalate}]_{\text{milled}}$ / $TiCl_4$ -TEA + 1,8-epoxy-p-methane

Table 2.8 Examples of precipitation catalysts (Yang, 1994)

Patent no.	Date	Company	Catalyst system
EP 86,472	1983	Montedison	(MgCl ₂ +EtOH+TiCl ₄ +diisobutylphthalate)/ TiCl ₄ -TEA+2-amino-2-methyl-1-propanol
EP 86,644	1983	Mitsui	(MgCl ₂ +EtOH+kerosene+emasol)/ TiCl ₄ +diisobutylphthalate/ TiCl ₄ -TEA+TMPIP
US 4,710,482	1987	Shell	(MgCl ₂ +MeOH)+Mg/MeOH+i-PrOH/diisobutylphthalate+TiCl ₄ +PhCl/phthaloylchloride-(TEA+Ph ₂ Si(OMe) ₂)
JP 01,256,503	1989	Toho Titanium	(MgCl ₂ +ethyl-p-anisate+decane+Ti(OBu) ₄ +2-ethylhexanol+heptane/dibutylphthalate+heptane/TiCl ₄ -(TEA+Ph ₂ Si(OMe) ₂)
DE 3,819,577	1989	Hoechst	(MgCl ₂ +2-ethylhexanol+phthalicanhydride+decane)+ TiCl ₄ /diisobutylphthalate/TiCl ₄ -TEA+PhSi(OEt) ₃ +cyclohexyldimethoxymethylsilane
JP 02,170,803	1990	Tokuyama soda	(MgCl ₂ +2-ethylhexanol+decane)+ phthalicanhydride/TiCl ₄ /diisobutylphthalate/TiCl ₄ -TEA (prepolymerization)-(TEA+Ph ₂ Si(OMe) ₂)
JP 0,280,407	1990	Showa Denko	(MgCl ₂ +2-ethylhexanol+decane)+ phthalicanhydride/TiCl ₄ /diisobutylphthalate/TiCl ₄ -TEA+1,3-dimethoxy-1,1,3,3-tetraisopropylidisiloxane

magnesium dialkoxides (Yang 1994). Some patent examples are shown in Table 2.9. Summaries of this type of catalysts were given by Karol (1984).

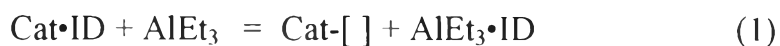
Table 2.9 Examples of MgCl_2 -rich catalysts (Yang, 1994)

Patent no.	Date	Company	Catalyst system
EP 245,854	1987	Sumitomo	$\text{BuMgCl} + \text{Bu}_2\text{O} + \text{Ti}(\text{OBu})_4 + \text{PhOH} +$ heptane/diisobutylphthalate+PhCl/ $\text{Bu}_2\text{O} + \text{TiCl}_4 + \text{PhCl} - \text{TEA} + \text{PhSiEt}_3$
WO 8,706,945	1987	Toho Titanium	$\text{Mg}(\text{OEt})_2 + \text{toluene} + \text{TiCl}_4 / \text{dibutyl-}$ phthalate/toluene/ $\text{TiCl}_4 + \text{toluene} /$ heptane-TEA+PhSi(OEt) ₃
BE 1,000,160	1988	Neste Oy	$(\text{Et}_2\text{Mg} / \text{sec-BuMgBu} + \text{Ph}_2\text{Si}(\text{OH})_2) +$ $\text{TiCl}_4 + \text{diisobutylphthalate} / \text{TiCl}_4 -$ TEA+Ph ₂ Si(OMe) ₂
DE 3,730,022	1989	BASF	$(\text{C}_8\text{H}_{17}\text{MgBu} + \text{SiO}_2 + \text{heptane})_{\text{milled}} / \text{HCl} /$ EtOH/ $\text{TiCl}_4 + \text{dibutylphthalate} / \text{TiCl}_4$ +PhEt-TEA+MeC ₆ H ₄ Si(OMe) ₃ +PP
JP 01,236,204	1989	Idemitsu	$[\text{Mg}(\text{OEt})_2 + \text{dibutylphthalate}] + \text{TiCl}_4 /$ MeOCMe ₃ +Al(CH ₂ CHMe ₂) ₃ + heptane-Al(CH ₂ CHMe ₂) ₃ +dicyclo- hexylphthalate
US 4,876,230	1989	Shell	$[\text{Mg}(\text{OMe})_2 \cdot 4\text{MeOH} / \text{MeOH-}$ extraction/ $\text{TiCl}_4 + \text{diisobutylphthalate}$ +PhCl - TEA+DIBDMS
US 4,927,797	1990	Fina	$[\text{Mg}(\text{OEt})_2 + \text{TiCl}_4 + \text{toluene}] / \text{dibutyl-}$ phthalate/ $\text{TiCl}_4 + \text{toluene} - \text{TEA} +$ cyclohexyldimethoxymethylsilane

2.3 Cocatalysts

Cocatalyst plays a key role in the polymerization of α -olefins. It has influenced on polymerization kinetics, activity and the stereospecificity of polymer products by the type of alkyl, its absolute and ratio (Al/Ti) concentrations. Yang and Hsu (1995a) depicted the dependencies of activity and isotactic index on the Al/Ti ratio for the MgCl_2 /dioctylphthalate (DOP)/ TiCl_4 -alkyl aluminum catalyst system. For catalyst with TEA as cocatalyst, the maximum activity is around $\text{TEA/Ti} = 50$, while the isotactic index decreases slightly with an increasing TEA/Ti ratio (Figure 2.2). On the other hand, with Triisobutylaluminum (TIBA) as a cocatalyst, the activity increases with the TIBA/Ti ratio up to $\text{TIBA/Ti} = 70$ and then remains unchanged, whereas the isotactic index follows a similar trend as that of TEA (Figure 2.3). Dumas and Hsu (1989) demonstrated, based on a multiple active site model, that the optimum activity behavior may occur because sites of widely different activities also have different rates of deactivation. Similar effects of TEA were also observed in other catalyst systems by Park and Lee (1992).

Soga *et al.* (1988) reported only a slight decrease or no change in isotacticity with regard to Al/Ti ratio for a MgCl_2 -supported catalyst containing di-n-butylphthalate as an internal base. Sacchi *et al.* (1991, 1996) proposed some equilibrium reaction model with the following.



where $\text{Cat}-[\]$ is a free site, ID is an internal donor, and ED is an external donor.

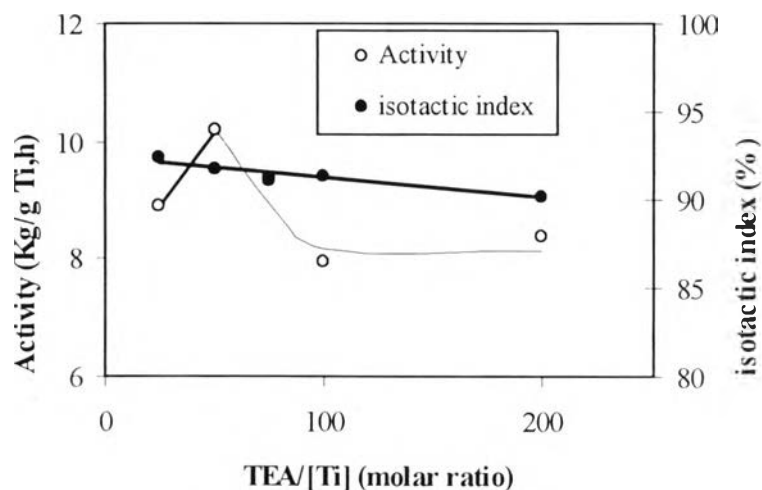


Figure 2.2 Effect of TEA/Ti ratio on activity and isotactic index for the $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ -alkyl aluminum catalyst system. Polymerization conditions: $[\text{Ti}] = 0.12 \text{ mmol/L}$; polymerization temperature = 50°C ; $\text{Al}/\text{Ti} = 50$; propene partial pressure 118 kPa; polymerization time = 1 h. (Yang and Hsu, 1995a)

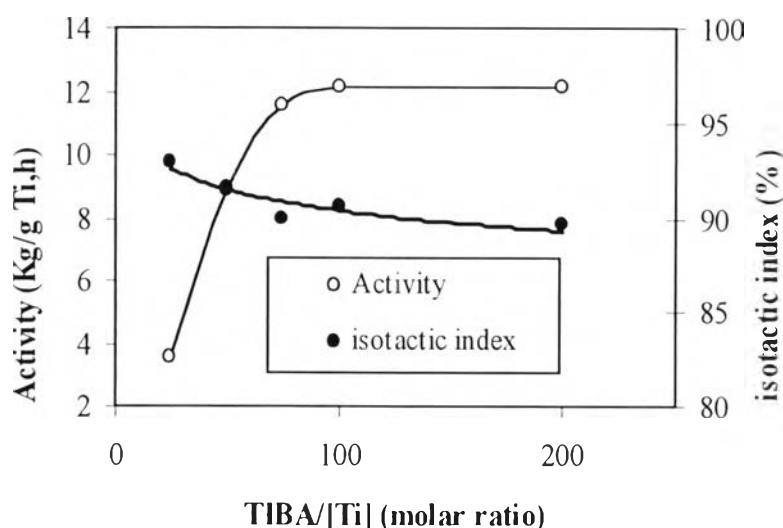


Figure 2.3 Effect of TIBA/Ti ratio on activity and isotactic index for the $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ -alkyl aluminum catalyst system. Polymerization conditions: $[\text{Ti}] = 0.12 \text{ mmol/L}$; polymerization temperature = 50°C ; $\text{Al}/\text{Ti} = 50$; propene partial pressure 118 kPa; polymerization time = 1 h. (Yang and Hsu, 1995a)

Equilibrium 1 is always present, even in the absence of the external donor. The free site produced could be aspecific or already stereospecific. Equilibrium 2 is also always present, the possibility of formation of the complex between AlEt_3 and the external donors is important in order to reduce the concentration of the free donor which can act as a poison. Therefore, equilibrium 3 can be neglected for the interactions of the free donor with the catalyst and only those of the donor/aluminum alkyl complex are considered. In principle it can react with the free site in two different ways. According to equilibrium 4, the complex itself would be coordinated to the catalyst surface. According to equilibrium 5, the complex releases the donor which is absorbed by the free site.

2.4 Lewis Base

To improve stereospecificity of MgCl_2 -supported catalysts in propene polymerization, many types of Lewis base including alcohol, ester, amines, and silanes have been used as additives during polymerization. However, the external Lewis base often has an adverse effect on catalyst activity (Pino and Mülhaupt, 1980; Keii *et al.*, 1983). Surprisingly, some aromatic esters like ethyl benzoate were found to increase not only catalyst stereospecificity but also catalyst activity as well (Luciani *et al.*, 1980; Sacchi *et al.*, 1990). Much effort has been used to find better combinations of internal and external donors. A MgCl_2 -supported TiCl_4 catalyst containing an aromatic diester such as dialkyl phthalate as an internal donor and alkoxy silane or hindered amine as external donor was found to be most efficient (Monte and Cecchin, 1982; Yamamoto *et al.*, 1986; Kashiwa *et al.*, 1988; Hoppin and Tovrog, 1989; Proto *et al.*, 1990; Iiskola *et al.*, 1999; Shamsoum and Rauscher, 1999). Yang and Hsu (1995a) found that dimethoxydiphenyl silane (DMDPS) and 2,2,6,6-tetramethyl piperidine (TMPiP) show similar effects on activity and isotactic

index in the catalyst system containing a high level of phthaloyl dichloride (POC) complex which was formed by the reaction between TiCl_4 and DOP. The catalyst activity increases sharply with a small amount of DMDPS (Figure 2.4) or TMPIP (Figure 2.5), reaches a maximum at a molar ratio of about $\text{base/TEA} = 0.013\text{-}0.025$, and then remains fairly constant at high base concentrations. The isotactic index, on the other hand, increases initially with base concentration and then levels off. The increase in activity at low base concentrations has been witnessed by several other authors: Dumas and Hsu (1989) with $\text{MgCl}_2/\text{EB}/\text{TiCl}_4\text{-TEA}/\text{TMPIP}$ catalyst systems; Soga *et al.* (1988) with $\text{MgCl}_2/\text{di-n-butylphthalate}/\text{TiCl}_4\text{-TEA}/\text{phenyltriethoxysilane}$ (PTES); and Kang *et al.* (1998) with $\text{Mg}(\text{OEt})_2/\text{di-n-butylphthalate}/\text{TiCl}_4\text{-TEA}/\text{several external donor}$. In these catalyst systems, an increase in activity at low concentrations seems to be more affirmed than in other systems mentioned above. An increase in POC content should be induced by the complexation of TEA and the external base allowing the external base to incorporate more easily onto the catalyst.

A number of papers have been published concerning the role of Lewis base on propene polymerization (Pino and Mülhaupt, 1980; Barbé *et al.*, 1987; Morini *et al.*, 1996; Sacchi *et al.*, 1996). The general explanations for the roles of internal and external donors were discussed in many other authors (Keii *et al.*, 1983; Kashiwa, 1983; Yang and Hsu, 1995a) as follows.

Roles of internal donors:

- I) To prevent the coagulation of MgCl_2 particles during the milling process, resulting in an enhancement of the effective surface area
- II) To prevent the formation of non-stereospecific sites by adsorbing on the MgCl_2 surface, where TiCl_4 is supported to form non-stereospecific sites
- III) To take part in the formation of highly isospecific sites

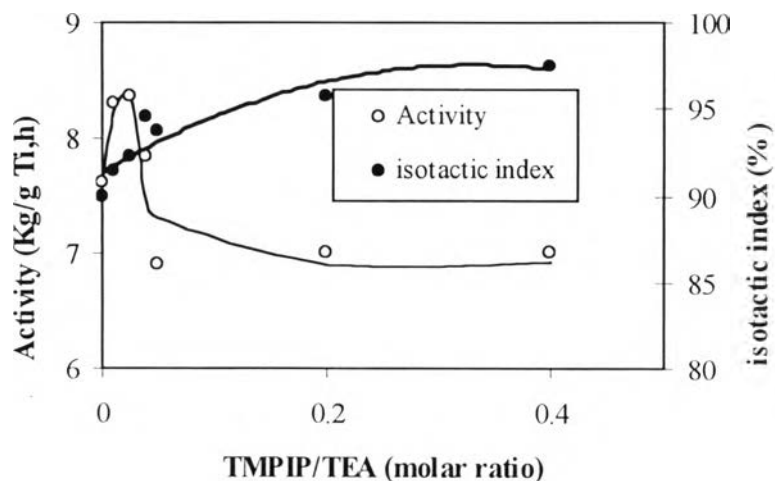


Figure 2.4 Effect of TMP/IP/TEA on activity and isotactic index for the $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ -alkyl aluminum catalyst system containing a high level of POC complex. Polymerization conditions: $[\text{Ti}] = 0.12 \text{ mmol/L}$; polymerization temperature = 50°C ; $\text{Al/Ti} = 50$; propene partial pressure 118 kPa; polymerization time = 1 h. (Yang and Hsu, 1995a)

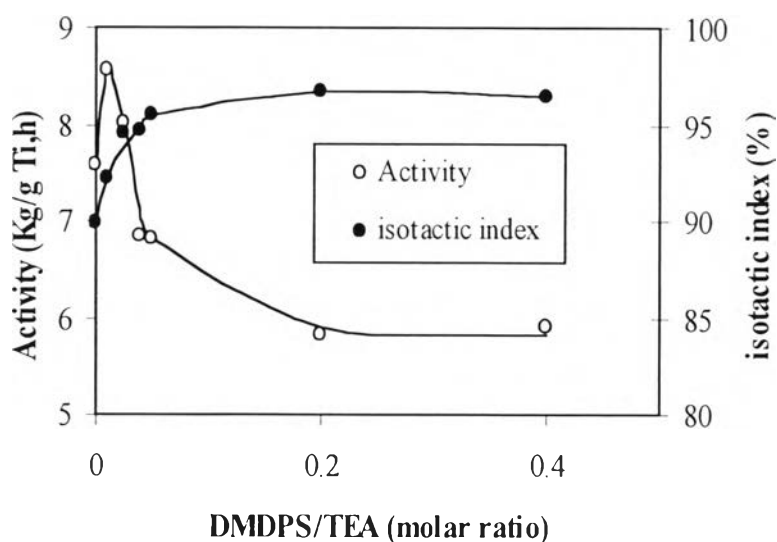


Figure 2.5 Effect of DMDPS/TEA on activity and isotactic index for the $\text{MgCl}_2/\text{DOP}/\text{TiCl}_4$ -alkyl aluminum catalyst system containing a high level of POC complex. Polymerization conditions: $[\text{Ti}] = 0.12 \text{ mmol/L}$; polymerization temperature = 50°C ; $\text{Al/Ti} = 50$; propene partial pressure 118 kPa; polymerization time = 1 h. (Yang and Hsu, 1995a)

IV) To be replaced by external donors, resulting in the formation of more isospecific sites.

Roles of external donors:

I) To poison non-stereospecific sites selectively

II) To convert non- stereospecific sites into highly isospecific sites

III) To convert isospecific sites into more highly isospecific sites

IV) To increases the reactivity of the isospecific sites.

Härkönen *et al.* (1990) suggested that the high performance external donor should have two or in some case three alkoxy groups and relatively large non-linear hydrocarbon groups or bulky non-aromatic groups such as isobutyls. The alkoxy groups should not be larger than ethoxy. Figure 2.6 shows the dependence of isotactic index of polymers on Al/Ti ratio in the catalyst systems with and without electron donor (Xu *et al.*, 1997). A similar variation of isotacticity of polypropylene with Al/Ti was observed by Barbé *et al.* (1987).

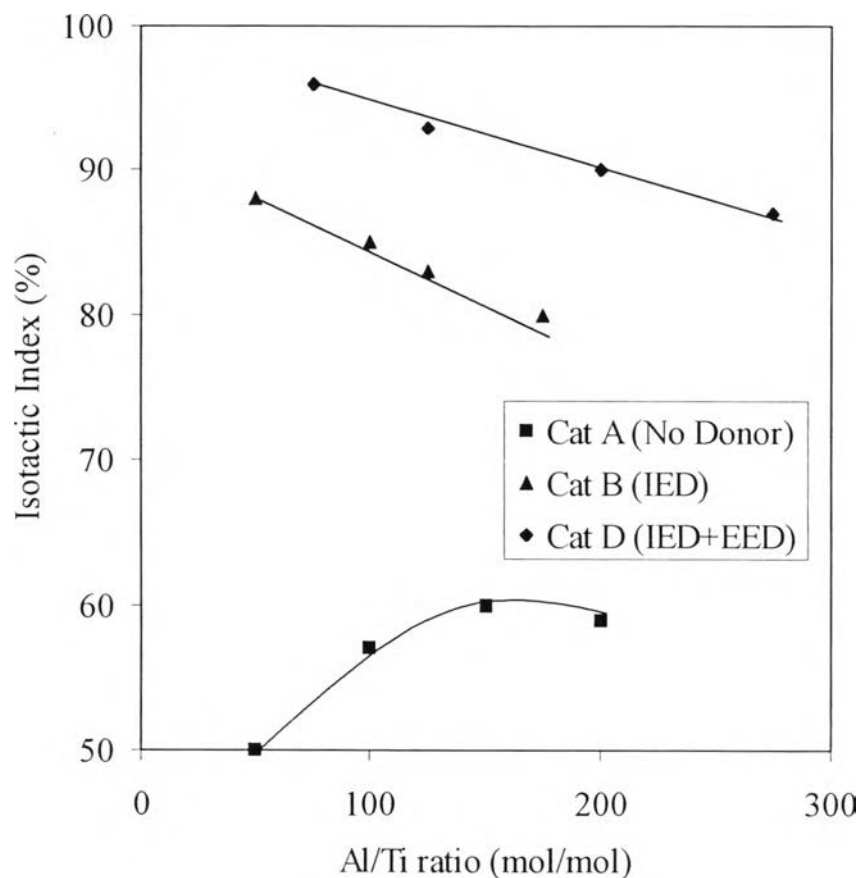
2.5 Polymerization Mechanism

Several attempts have been made to propose a mechanism that could be applied to all Ziegler-Natta catalyzed polymerizations. A number of papers on the polymerization mechanisms of Ziegler-Natta catalysts have been published (Corradini, *et al.*, 1989; Tiat and Watkins, 1989).

2.5.1 The Cossee Mechanism

It is well known that the two key steps in Ziegler-Natta catalyzed polymerization is the complexation between the monomer and the active center, followed by insertion into the growing polymer chain. In this mechanism, the cocatalyst acts as alkylating and reducing agent, and polymer

growth takes place via insertion of monomer into the transition metal-carbon bond.



CatalystA = $\text{TiCl}_4/\text{MgCl}_2\text{-AlEt}_3$

CatalystB = $\text{TiCl}_4/\text{MgCl}_2/\text{di-n-butylphthalate-AlEt}_3$

CatalystC = $\text{TiCl}_4/\text{MgCl}_2/\text{di-n-butylphthalate-AlEt}_3/\text{diphenyl-dimethoxysilane}$

Figure 2.6 Dependence of isotactic index of polymer on Al/Ti ratio (Xu *et al.*, 1997)

2.5.1.1 *The Active Center*

The active center in Ziegler-Natta catalysts is the transition metal-carbon bond of the transition metal complex that is formed by the interaction between components of the catalytic system.

2.5.1.2 *Two-steps 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.

Figure 2.7 shows monometallic polymerization mechanism, which was proposed by Cossee (1960, 1961), where X is a halogen ligand, R is a growing polymer chain or alkyl group, and the open squares indicate a ligand vacancy. In this model, the active site is composed of a transition metal atom having an octahedral configuration, with four chlorine ligands from the crystal lattice, an alkyl group introduced by the cocatalyst and a coordination vacancy. The coordination vacancies are required to ensure the electroneutrality of the crystal. This recreates the vacant coordination site at the site originally occupied by the polymer chain and the process continues with the growing polymer chain terminus flips from site to site. Step 4 is probably the weakest assumption of Cossee's model. In order to explain isotacticity, the polymer chain has to flip back to the position occupied before the monomer insertion step. Moreover, why the polymerization rate order relative to monomer concentration is higher than 1.0; why isospecific polymerization seems to have a higher propagation rate than non-specific polymerization; why the stereoregularity of the first inserted monomer seems to be lower than for the insertion of the rest; and why the copolymerization rates higher than homopolymerization rate of both comonomers (Ystenes, 1991).

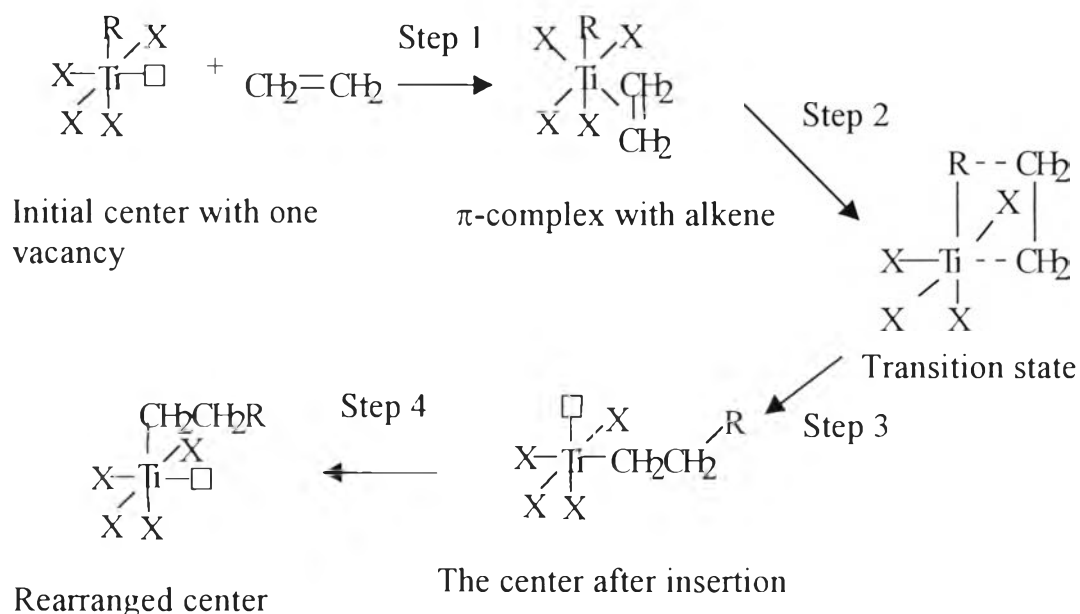


Figure 2.7 Proposed mechanism by Cossee (1960, 1961)

Although several alternative monometallic models have been proposed based on Cossee's model (Corradini, *et al.*, 1989; Tiat, and Watkins, 1989). There is no agreement about the general validity of these models, but it is generally accepted that Cossee's model provides the best represent to date for the mechanisms governing Ziegler-Natta polymerization.

2.5.2 The Trigger Mechanism

Recently the trigger mechanism was proposed by Ystenes (1991). It is a new concept to understand the polymerization of α -olefins with Ziegler-Natta catalysts. This mechanism is based on the interaction between two monomers in the transition state, where an incoming monomer triggers the insertion of a complexed monomer. Figure 2.8 shows the trigger mechanism. The main assumptions of this model are: (1) the monomer site is never free, it is always occupied by a monomer, since a new monomer will enter the site when the monomer that previously occupied this site is inserted in the growing

chain. (2) The complexed monomer will be inserted if and only if a new monomer is ready to complex. Hence the monomer site is protected from attack by Lewis bases. (3) Two monomer are associated with the active metal complex in the transition state. The trigger mechanism is able to predict polymerization rate dependent upon monomer concentration from first to second order, the increase in polymerization rate of ethylene upon adding propylene, and the first inserted monomer has a lower stereoregularity.

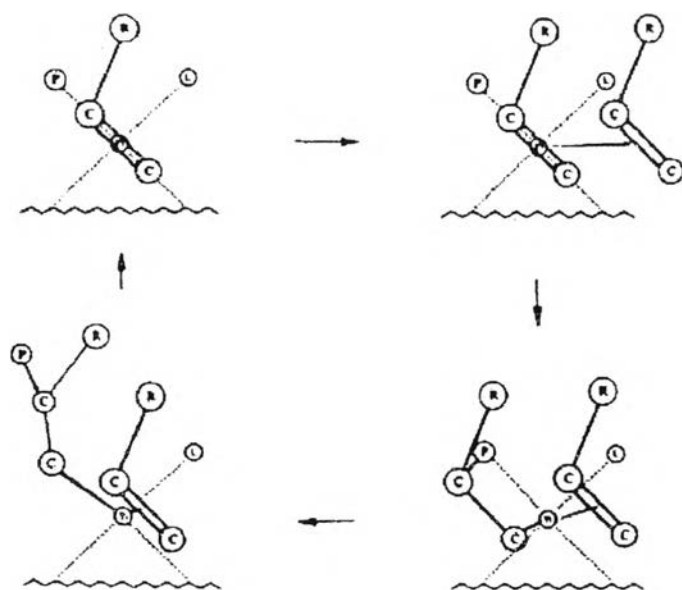


Figure 2.8 Proposed mechanism by Ystenes (1991)

2.6 Hydrogen

Hydrogen has been used as a modifier for controlling the molecular weight in the polymerization of ethene and α -olefins catalysed by titanium-based Ziegler-Natta catalysts. Lee and Jeong (1993) used the $\text{Mg}(\text{OEt})_2/\text{benzoyl chloride (BC)}/\text{TiCl}_4\text{-TEA}/\text{ED}$ catalyst system to study effects of hydrogen. They suggested that the effects of hydrogen on catalyst activity (rate enhancement) and isospecificity for the present catalyst system depend on the kind and amount of ED although the detailed mechanism is not yet known. For this catalyst system, the polymerization behavior was examined for various amounts of hydrogen with fixed amount of ED, methyl p-toluene (MPT) or phenyltriethoxysilane (PTES) as shown in Table 2.10. The model of active sites has been proposed by many workers for MgCl_2 -supported TiCl_4 catalyst and it has been suggested that three active sites having different isospecific sites are larger than that for the aspecific sites, so that the isospecific sites might produce high MW.

With MPT or PTES, the catalyst activity increases to a constant level with the amount of hydrogen. On the contrary, the isotactic index of PP decreases continually for MPT but is less dependent on the amount of hydrogen in the presence of PTES. The rate enhancement, shown as ratio A^{H}/A^0 , is found to be greater for PTES than for MPT; A^{H} is activity with hydrogen and A^0 that without hydrogen.

With fixed amount of ED, the melt flow rate (MFR) increases with amount of hydrogen as shown in Table 2.10. A decrease in MW caused by hydrogen is greater in the presence of PTES than MPT. The MW and molecular weight distributions (MWD) of PP obtained for various amounts of ED with fixed amount of hydrogen were measured by GPC and are given in Table 2.11.

Table 2.10 Effect of hydrogen pressure on the polymerization behavior for Mg(OEt)₂/benzoyl chloride (BC)/TiCl₄-TEA/ED catalyst system (Lee and Jeong, 1993)

Hydrogen Pressure Mpa	with MPT				With PTES			
	Act.*	II.†	MFR‡	A ^H /A ⁰ §	Act.*	II.†	MFR‡	A ^H /A ⁰ §
0	204.0	69.5	3.9	-	54.2	81.6	1.4	-
0.004	222.0	68.3	6.0	1.09	69.5	86.1	17.4	1.28
0.008	280.8	68.4	28.0	1.38	99.0	87.8	37.6	1.83
0.016	297.5	63.0	74.9	1.46	108.4	89.6	66.6	2.00
0.032	295.2	60.4	124.2	1.45	102.8	83.8	151.4	1.90
0.064	295.7	54.2	-	1.45	102.5	82.5	347.0	1.89

*Catalyst activity in kg of PP/(g of Ti-Hr).

†Isotactic index in wt%.

‡Melt flow rate in g/10min.

§Ratio of catalyst activity with hydrogen to that without hydrogen

Polymerization conditions; [TEA]=5.0 mmol/l, [ED] = [MPT] = [PTES] = 0.20mmol/l, propene pressure = 1.01 Mpa, 70°C, 2 h.

As well known, the number-average molecular weight (\overline{M}_n) increases with the amount of ED. In addition, $\overline{M}_n^H / \overline{M}_n^0$ i.e. the ratio of \overline{M}_n with hydrogen to that without hydrogen, increases with the amount of MPT but decreases for PTES. This result suggested that the catalyst with PTES is more sensitive to hydrogen than that with MPT and the chain transfer to hydrogen is also affected by ED.

Table 2.11 Effect of ED and hydrogen on molecular weight of PP with Mg (OEt)₂/benzoyl chloride (BC)/TiCl₄-TEA/ED catalyst system (Lee and Jeong, 1993)

ED	[ED]/[TEA] in mole ratio	Amount of hydrogen (Mpa)	\overline{M}_n	$\overline{M}_w / \overline{M}_n$	$\overline{M}_n^H / \overline{M}_n^0$ *
MPT	0	0	40,800	5.72	-
	0.047	0	48,600	5.48	-
	0.184	0	58,200	7.43	-
	0	0.016	23,100	4.57	0.57
	0.047	0.016	32,000	4.63	0.66
	0.184	0.016	41,800	5.94	0.72
PTES	0	0	40,800	5.72	-
	0.047	0	61,500	6.55	-
	0.184	0	85,300	5.69	-
	0	0.016	23,100	4.57	0.57
	0.047	0.016	35,600	3.96	0.58
	0.184	0.016	41,100	3.59	0.48

*Ratio of \overline{M}_n with hydrogen to that without hydrogen. Polymerization condition; [TEA]=5.0mmol/l, propene pressure=1.10 MPa, hydrogen pressure=0.016 MPa, 70°C, 2 h.