CHAPTER II
LITERATURE REVIEW

2.1 Polyolefin

Polyolefin is the largest class of organic thermoplastic polymers, commonly referred to polyalkenes. As polyolefin materials are used in consumer goods, structural plastics, food packaging and industrial products, they are also called "commodity thermoplastics". Heterogeneous transition metal catalysts (Ziegler-Natta catalysts, Phillips catalysts) for olefin polymerization were discovered in 1950s. Since then, these types of catalysts have been used in polyolefin industry, and now polyolefin has become the champions of commodity plastics with global production exceeding 100 million tons/year (Makio and Fujita, 2012). The development of the catalysts for olefin polymerization has been one of the interests. Although Ziegler-Natta catalysts have high activities, their products have variable physical properties due to the different active sites in the catalysts (Davis, 2012). With the need to control the homogeneity of the obtained polymers, a new type of catalyst for olefin polymerization was investigated. Metallocene catalysts are the new catalyst with single active site, thus can control the polymerization with desirable properties (Davis, 2012).

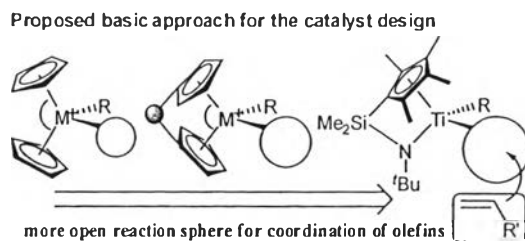## 2.2 Heterogeneous Ziegler-Natta catalysts

Heterogeneous Ziegler-Natta catalysts are currently widely used in industry for olefin polymerization and copolymerization. This type of catalysts is based on a mixture of transition metal commonly a titanium compound such as $TiCl_4$ as catalyst, an alkali metal such as $AlEt_3$, $AlEt_2Cl$, and Al^iBu_3 as cocatalyst and $MgCl_2$ as catalyst support. The $MgCl_2$-supported $TiCl_4$ catalyst ($TiCl_4/MgCl_2$-$AlEt_3$) exhibited high activity for propylene polymerization but the problem was that co-production of the atactic component increased simultaneously. An electron donor (ED), such as ethyl benzoate, was introduced to the catalyst to suppress the formation of atactic component and also improved stereoselectivity (Makio and Fujita, 2012).

2.3 Metallocene catalysts

Metallocene catalysts are positively charged metal ions, most commonly titanium or zircronium, sandwiched between two negatively charged cyclopentadienyl rings. The original metallocene catalyst systems contained $(C_5H_5)_2TiCl_2$ (usually depicted as Cp_2TiCl_2) and a dialkylaluminum chloride cocatalyst, such as AlMe$_2$Cl and AlEt$_2$Cl (Reichert and Meyer, 1973). However, these systems show only moderate activities in olefin polymerization. In 1976, Sinn and Kaminsky discovered the use of methylaluminoxane (MAO) as cocatayst for metallocene system. Activation of $CpZrR_2$ (R = Cl, Me) with MAO led to exceedingly active catalyst for ethylene polymerization as well as propylene and higher α-olefins polymerization (Kaminsky, 1981; Herwig and Kaminsky, 1983; Kaminsky *et al.,* 1983). In addition to this high activity, metallocene catalysts are chemically uniform, single site catalysts and therefore structurally uniform polymers can be obtained (Makio and Fujita, 2012).

2.4 Non-bridged half-titanocenes containing anionic ancillary donor ligands

It has been recognized that the catalysts exhibiting remarkable activities with better comonomer incorporations should be desired for the successful design of an efficient transition metal catalyst for ethylene (co)polymerizations. It has been reported that bridged (*ansa*) metallocene-type complexes generally show better comonomer incorporation than the nonbridged (unbridged) analogues in ethylene/α-olefin copolymerization (Brintzinger *et al.,* 1995; Kaminsky, 1996 and 1997 and Suhm *et al.,* 1998). The fact has been explained as that the bridged metallocenes possess rather large coordination space compared to the nonbridged analogues, allowing better accessibility for (rather) bulky α-olefins (Scheme 2.1). Linked half-titanocenes containing amide ligand, [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$. (1) so called "constrained geometry catalyst (CGC)", have also been known to exhibit efficient comonomer incorporation (Scheme 2.1) (Okuda *et al.,* 1995; Carpeneth *et al.,* 1996; McKnight *et al.,* 1997 and Harrington and Crowther 1998).

Proposed basic approach for the catalyst design

more open reaction sphere for coordination of olefins

Scheme 2.1 Basic proposed concept for the catalyst design (Brintzinger *et al.,* 1995; Kaminsky, 1996 and 1997 and Suhm *et al.,* 1998)

Efficiencies in the ethylene copolymerizations can be evaluated by the monomer reactivity ratio (r_E), which is defined as $r_E = k_{EE}/k_{EC}$ (E = ethylene, C = comonomer, Scheme 2.2) (Nomura, 2009), and as exemplified in Table 2.1 (Soga *et al.,* 1996; Suhm *et al.,* 1997 and 1998), the r_E value decreases in the order: $Cp_2ZrCl_2 \gg$ *rac*-Me$_2$Si[benz(e)Ind]$_2$ZrCl$_2 >$ [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC). It is also known that the r_E values by ordinary metallocenes were dependent upon the polymerization temperature, whereas the $r_E \cdot r_C$ ($r_E \cdot r_0$) values were ca. 1.0, indicating that the copolymerizations proceed in a random manner (or comonomer incorporations are random) (Brintzinger *et al.,* 1995; Kaminsky and Arndt, 1997 Suhm 1998; McKnight and Waymouth, 1998). The facts would also support an assumption that *bridge constrains more open coordination sphere for bulky α-olefins*, although the coordination sphere should not be the exclusive factor for better comonomer incorporation based on recent reports (Kunz *et al.,* 2002[a] and 2002[b]; Hung and Waymouth, 2005).
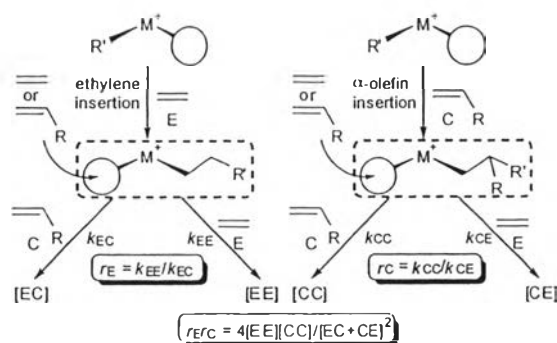
Scheme 2.2 Definition of r_E, r_C values (E = ethylene, C = comonomer) (Nomura, 2009).

Non-bridged half-titanocenes of the type, Cp'TiX$_2$(Y) (Cp' = cyclopentadienyl group; Y = anionic donor ligand such as aryloxo, ketimide, phosphinimide, iminoimidazolidide etc.; X = halogen, alkyl), as shown in Scheme 2.3 (Nomura *et al.*, 2007), have been considered as promising candidates for new efficient catalysts (for example, Nomura *et al.*, 1998^a, 1998^b, 2000, 2001, 2004 and 2007; Zhang *et al.*, 2000; Tamm *et al.*, 2004 and Stephen, 2005), because, as described below, these complex catalysts display unique characteristics especially for synthesis of new polymers (Nomura *et al.*, 2002-2007) that cannot be prepared (or are very difficult to be prepared) by ordinary catalysts such as Ziegler-Natta, metallocenes (Brintzinger *et al.*, 1995; Kaminsky and Arndt, 1997; Suhm, 1998), 'constrained geometry' type catalysts (CGC) (McKnight and Waumouth, 1998; Cano and Kunz, 2007). There is a reveal in 1998 by Nomura *et al.* that half-titanocenes containing an aryloxo ligand of the type, Cp'TiCl$_2$(OAr) (Cp' = cyclopentadienyl group; OAr = aryloxo group, O-2,6-^{i}Pr$_2$C$_6$H$_3$ etc.), exhibited not only notable catalytic activities for olefin polymerization, but also for efficient 1-butene incorporation in ethylene/1-butene copolymerization (Nomura *et al.*, 1998). In the same year, there were several reports concerning synthesis of Cp'TiX$_2$(Y) and their use as catalysts for ethylene polymerization (Richter *et al.*, 1998; Doherty *et al.*, 1998; Sita and Babcock, 1998) . After these reports, many examples were reported describing the synthesis of complexes of this type and for use as olefin polymerisation catalysts, especially for ethylene polymerization.

Nomura *et al.* already demonstrated that the half-titanocenes containing aryloxo, ketimide ligands display promising characteristics especially for copolymerization of ethylene not only with monoolefins containing bulky substituent such as vinylcyclohexane (Nomura and Itagaki, 2005), 3-methyl-1-pentene (Kakinuki *et al.*, 2009), *tert*-butylethylene (Khan *et al.*, 2009), but also with 2-methyl-1-pentene (Nomura *et al.*, 2005 and Itagaki *et al.*, 2007), styrene (Nomura *et al.*, 2000). These complexes are also effective for the synthesis of cyclic olefin copolymers by ethylene copolymerization (Nomura, 2008), as well as for the introduction of functional groups into polyolefins in efficient manners (Nomura and Kitiyanan, 2008). It turned out that an efficient catalyst for the desired (co)polymerization can be modified by simple replacement of both the cyclopentadienyl fragment (Cp') and the anionic donor ligands (Y) (Nomura *et al.*, 2007). The ligand modifications (sterically and/or

electronically) should be easier than those in the ordinary bridged half-metallocene (constrained geometry) type complexes, because the synthesis generally requires short synthetic steps and affords the desired derivatives in relatively high yields; this should be considered as a distinct advantage for using these types of complexes.

Table 2.1 Typical r_E and r_O values in ethylene/1-octene copolymerisation using various group 4 transition metal complex catalysts.[a]

complexes	$r_E{}^b$	$r_O{}^b$	$r_E{\cdot}r_O{}^b$
Cp_2ZrCl_2	32.8	0.05	1.17
rac-$Me_2Si(Ind)_2ZrCl_2$	18.9	0.014	0.27
rac-$Me_2Si(Benz[e]Ind)_2ZrCl_2$	10.7	0.076	0.81
rac-$Me_2Si(2$-MeBenz[e]Ind$)_2ZrCl_2$	10.1	0.118	1.2
rac-$Me_2Si(2$-MeBenz[e]Ind$)_2ZrCl_2$ [c]	8.16	0.14	1.14
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$	4.1	0.29	1.19

[a]Cited from reference 11c (in toluene at 40 °C). [b]Shown in Scheme 2.1, $r_E{\cdot}r_O$ = $4[EE][OO]/[EO]^2$ (E = ethylene, O = 1-octene), r_E = k_{EE}/k_{EO} = $[O]_0/[E]_0{\times}2[EE]/[EO+OE]$, r_O = k_{OO}/k_{OE} = $[E]_0/[O]_0{\times}2[OO]/[EO+OE]$ ($[E]_0$, $[O]_0$: Initial monomer concentration). [c]Cited from Soga et al., 1996.
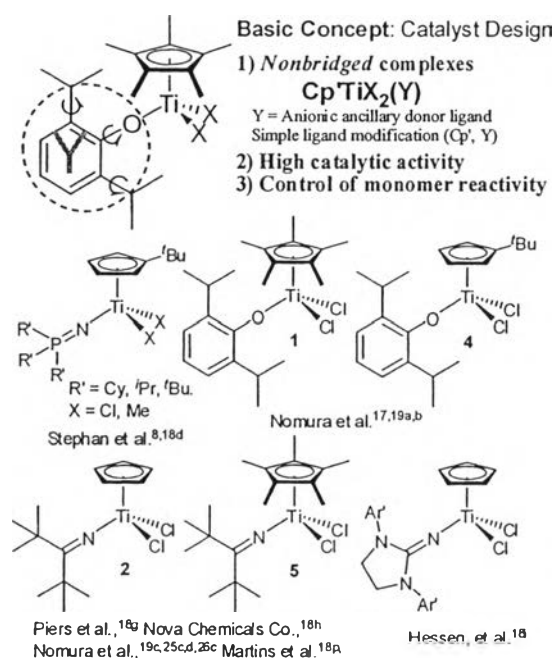
Scheme 2.3 Selected half-titanocenes containing anionic ancillary donor ligands as effective catalyst precursors for ethylene (co)polymerization (Nomura et al., 2007).

2.4.1 Copolymerization of ethylene with linear α-olefins by non-bridged half-titanocenes containing anionic ancillary donor ligands (Nomura, 2009)

Table 2.2 summarizes selected results in copolymerizations of ethylene with α-olefins using $Cp*TiCl_2(O-2,6-^iPr_2C_6H_3)$ (1), $CpTiCl_2(N=C^tBu_2)$ (2), and the constrained geometry catalyst (CGC), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (3), in the presence of MAO cocatalyst. The Cp*-aryloxo analogue (1) exhibited remarkable catalytic activities for copolymerization of ethylene with 1-butene (Nomura *et al.*, 1998) and 1-hexene (Nomura *et al.*, 2000 and 2001), affording high molecular weight copolymers with uniform compositions; the 1-hexene contents in the resultant copolymers by 1 were close to those by 3 under the same conditions. The observed catalytic activities (calculated from the polymer yields) by 1 were higher than those by 3, whereas the molecular weights in the resultant copolymers prepared by 3 were higher than those prepared by 1. It should be noted that the activity by the Cp*-aryloxo analogue (1) increased remarkably upon increasing the 1-hexene concentration, whereas the activity with the constrained geometry catalyst (3) decreased upon increasing 1-hexene concentration (Nomura *et al.*, 2001). A similar trend was observed in the copolymerizations with 1-pentene, 1-dodecene (Kakinuki *et al.*, 2009).

Table 2.2 Selected results in copolymerization of ethylene (E) with 1-pentene (PEN), 1-hexene (HEX) 1-dodecene (DD) by $Cp*TiCl_2(O-2,6-^iPr_2C_6H_3)$ (1), $CpTiCl_2(N=C^tBu_2)$ (2), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (3) - MAO catalyst systems.[a]

complex (μmol)	comonomer[b] / M	E / atm	temp. / °C	activity[c]	$M_n{}^d$ ×10^{-5}	$M_w/$ $M_n{}^d$	cont.[e] / mol%
1 (0.02)	PEN (1.52)	6	25	104000	1.85	1.90	36.5
2 (0.01)	PEN (1.52)	6	25	118000	7.23	1.91	29.1
1 (0.08)[f]	HEX (0.73)	5	40	83200	2.12	1.80	28.7
1 (0.08)[f]	HEX (0.73)	7	40	103000	2.30	1.98	24.6
1 (0.07)[f]	HEX (1.45)	7	40	263000	1.80	1.87	38.1
3 (0.60)[f]	HEX (0.73)	5	40	9490	3.63	2.05	30.0
3 (0.60)[f]	HEX (0.73)	7	40	14600	5.17	2.30	23.7
3 (0.65)[f]	HEX (1.45)	7	40	6960	3.98	2.21	39.4
1 (0.01)	DD (0.75)	6	25	230000	1.87	1.99	19.2
2 (0.01)	DD (0.75)	6	25	123000	4.84	1.97	15.5
3 (0.10)	DD (0.75)	6	25	24800	3.91	2.09	19.2

[a]Cited from Kakinuki et al., 2009, conditions: toluene and comonomer total 30 mL, dried MAO (prepared by removing toluene and AlMe$_3$ from the ordinary MAO) 3.0 (or 2.0) mmol, 25 °C, 10 min. [b]Initial comonomer concentration in mmol/mL. [c]Activity = kg-polymer/mol-Ti·h. [d]GPC data in o-dichlorobenzene vs polystyrene standards. [e]Comonomer contents estimated by ^{13}C NMR spectra. [f]Cited from Nomura et al., 2001, polymerisation for 6 (or 4) min.

The $^tBuC_5H_4$-aryloxo analogue, $(^tBuC_5H_4)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (4), exhibited better 1-hexene incorporation than 1 under the same conditions, whereas the $^tBu_2Cp$-aryloxo analogue, $(^tBu_2C_5H_3)TiCl_2(O-2,6-^iPr_2C_6H_3)$, showed less efficient 1-hexene incorporation than 1; the cyclopentadienyl fragments (Cp') thus affect the 1-hexene incorporation. The Cp-ketimide analogue (2) also exhibited remarkable catalytic activities in the copolymerizations (Nomura et al., 2004), but the comonomer incorporations were less efficient than those by 1 and 3. This suggests that the comonomer incorporation was also affected by the anionic donor ligand employed.

The activities by the Cp*-ketimide analogue, Cp*TiCl₂(N=C'Bu₂) (5), were lower than the Cp-ketimide analogue (2) under the same conditions (Hung and Waymouth, 2005), whereas no distinct differences were observed in the 1-hexene incorporation (Nomura et al., 2004); 5 exhibited better catalyst performance than 2 under high temperature (160 °C) and high pressure (1500 psi, 102 atm), continuous solution polymerization conditions (McMecking et al., 2000).

2.4.2 Copolymerization of ethylene with cyclic olefins by non-bridged half-titanocenes containing anionic ancillary donor ligand (Nomura, 2009)

It has been known that certain cyclic olefin copolymers (COCs) are amorphous materials with a promising combination of high transparency in the UV-Vis region along with humidity-, and heat-resistance (high glass transition temperature, T_g) (Kaminsky, 1994; Cherdon et al., 1994; Dragutan and Streok, 2000; Kaminsky and Beulich, 2001). Three processes such as (1) ring-opening metathesis polymerization (ROMP) of multi-cyclic olefins and the subsequent hydrogenation, (2) coordination copolymerization of ethylene with cyclic olefins, (3) homopolymerization of cyclic olefins, are generally adopted for the practical production of COCs. In particular, the copolymerization route seems promising, because the desired properties (glass transition temperature, T_g, etc.) should be tuned by their compositions (cyclic olefin contents etc.) as well as their microstructures (including tacticity).

Many examples were thus known for the copolymerization of ethylene with norbornene (NBE) using ordinary metallocenes (for example, Ruchatz and Fink, 1998; Pavasoli et al., 1999; Tritto et al., 2000-2002), linked half-titanocenes (so called constrained geometry type) (for example, Harrington and Crowther, 1998; Thorshaug et al., 2002; Hasan et al., 2004 and 2005; Cai et al., 2006), nonbridged half-titanocenes (Nomura et al., 2003, 2006 and 2007; Wang et al., 2005), and other so-called non-metallocenes (Altamura and Grassi, 2001;. However, successful examples for the efficient synthesis of random, high molecular weight copolymers with high NBE contents (>50 mol%), which possess high T_g (>150°C), were limited. This is not only because both the activity and the molecular weights for the copolymer generally decrease upon increasing NBE contents, but also because the microstructure in the copolymer possessed few NBE repeat units and contained

alternating ethylene-NBE sequences in addition to the isolated NBE units due to the difficulty for repeated insertion of NBE.

In 2003, Nomura and co-workers reported that (indenyl)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (6) exhibited better NBE incorporation than the Cp*-aryloxo analogue (1), the 1,2,4-Me$_3$C$_5$H$_2$-aryloxo analogue, and the constrained geometry catalyst (CGC, 3), affording random copolymers with high NBE contents (Scheme 2.4). The catalytic activity by the indenyl-aryloxo analogue initially increased upon increasing the NBE concentration charged, although the activity generally decreased upon increasing the NBE concentration.
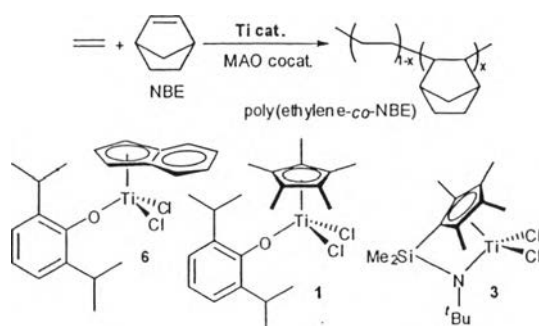
Scheme 2.4 (Nomura et al., 2003)

The same group recently reported that the Cp-kemitide analogue, CpTiCl$_2$(N=C^{t}Bu$_2$) (2), exhibits both remarkable catalytic activity and efficient NBE incorporation for ethylene/NBE copolymerization (Nomura et al., 2006). As shown in Table 2.3, the activity increased upon increasing in initial NBE concentration, whereas the activities by other catalysts decreased upon increasing in NBE concentration. Note that the activity by 2 increased at higher temperature (40, 60 °C) accompanied by increasing NBE content in the copolymer (due to a reduction in ethylene concentration in the mixture), and the activity did not decrease at least for 30 min. The resultant copolymers possessed high molecular weights with unimodal molecular weight distributions as well as with single compositions. The efficient synthesis of high molecular weight copolymers with high NBE contents (58.8-73.5 mol%) could therefore be attained upon increasing the NBE concentration at low ethylene pressure (2 atm).

Both the activities and the NBE incorporations in the copolymerization by 2 were not strongly affected by the Al cocatalyst employed (MAO, MMAOs), and the fact is a unique contrast to that reported in the copolymerization by [Me$_2$Si(fluorenyl)(N$'$Bu)]TiMe$_2$ in which both the activity and the NBE incorporation are highly dependent upon the Al cocatalyst employed (Hasan *et al.*, 2004). It is thus clear that these observed facts are significantly unique compared to those previously demonstrated in the copolymerization using ordinary metallocenes or linked half-titanocenes (Nomura *et al.*, 2006).

Cp*TiCl$_2$(N=C$'$Bu$_2$) (**5**) also showed high catalytic activity for the copolymerization, but the activity decreased upon increasing the NBE concentration. The copolymerization by CpTiCl$_2$[N=C($'$Bu)Ph], CpTiCl$_2$(N=CPh$_2$), Cp*TiCl$_2$(N=CPh$_2$) - MAO catalyst systems showed low catalytic activities, and the resultant (co)polymers possessed a mixture of low and high molecular weight polymers (Nomura *et al.*, 2007).

Table 2.3 Copolymerization of ethylyne with norbornene (NBE) by $Cp^*TiCl_2(O-2,6-^iPr_2C_6H_3)$ [Cp' = Cp* (1), indenyl (6)], $CpTiCl_2(N=C^tBu_2)$ (2), $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (3), $[Me_2Si(indenyl)_2]ZrCl_2$ - MAO catalyst systems.[a]

cat. (μmol)	temp. / °C	ethylene / atm	NBE[b] / mmol/mL	activity[c]	M_n^d ×10^{-4}	M_w/M_n^d	NBE[e] / mol%
$Cp^*TiCl_2(O-2,6-^iPr_2C_6H_3)$ (1) (0.2)	25	4	1.0	2640	29.6	1.46	21.7
$(indenyl)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (6) (0.2)	25	4	1.0	2300	5.87	1.82	35.2
$(indenyl)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (6) (0.2)[f]	25	2	2.5	678	3.91	1.58	58.8
$(indenyl)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (6) (0.2)[f]	25	2	5.0	126	0.78	2.42	60.1
$CpTiCl_2(N=C^tBu_2)$ (2) (0.1)	25	4	-	5880	45.2	2.30	-
$CpTiCl_2(N=C^tBu_2)$ (2) (0.02)	25	4	0.2	21600	70.6	1.85	17.8
$CpTiCl_2(N=C^tBu_2)$ (2) (0.02)	25	4	1.0	40200	71.9	2.92	40.7
$CpTiCl_2(N=C^tBu_2)$ (2) (0.02)	40	4	1.0	48900	62.0	2.37	45.9
$CpTiCl_2(N=C^tBu_2)$ (2) (0.02)	60	4	1.0	194000	47.5	2.20	51.2
$CpTiCl_2(N=C^tBu_2)$ (2) (0.01)[f]	25	2	2.5	90000	32.3	2.09	58.8
$CpTiCl_2(N=C^tBu_2)$ (2) (0.01)[f]	25	2	5.0	85800	34.0	2.00	65.8
$CpTiCl_2(N=C^tBu_2)$ (2) (0.02)[f]	25	2	10.0	31500	44.4	2.01	73.5
$[Me_2Si(indenyl)_2]ZrCl_2$ (0.10)	25	4	1.0	4860	22.9	2.37	29.5
$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (3) (0.50)	25	4	1.0	2000	12.8	2.15	26.5

[a]Cited from reference 37c, conditions: toluene+NBE total 50 mL, MAO white solid (prepared by removing AlMe$_3$, toluene from PMAO) 3.0 mmol, 10 min. [b]NBE concentration charged (mmol/mL). [c]Activity in kg-polymer/mol-M·h (M = Ti, Zr). [d]GPC data in *o*-dichlorobenzene vs polystyrene standards. [e]NBE content (mol %) estimated by ^{13}C NMR spectra. [f]Conditions: toluene+NBE total 10 mL.
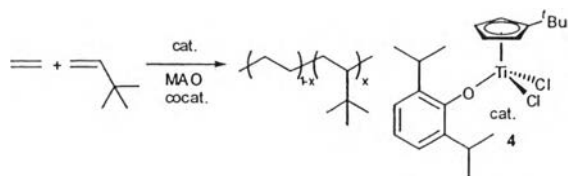
2.4.3 Copolymerization of ethylene with *tert*-butylethylene by non-bridged half-titanocenes containing anionic ancillary donor ligand (Nomura, 2009)

Table 2.4 Copolymerization of ethylene with *tert*-butylethylene (TBE) using Cp'TiCl$_2$ (O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp*, ^{t}BuC$_5$H$_4$, 1,2,4-Me$_3$C$_5$H$_2$], Cp'TiCl$_2$(N=C^{t}Bu$_2$) [Cp' = Cp, Cp*, ^{t}BuC$_5$H$_4$], [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$, and Cp$_2$ZrCl$_2$ – MAO catalyst systems.[a]

complex (μmol)	activity[b]	M_n^c ×10^{-4}	M_w/ M_n^c	cont.[d] (mol%)
Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (1) (0.2)	2880	20.4	2.0	1.7
(^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (1.0)	1130	5.31	2.1	6.3
(^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (1.0)[e]	552	2.23	2.8	9.5
CpTiCl$_2$(N=C^{t}Bu$_2$) (2) (0.4)	1880	13.9	1.9	trace
Cp*TiCl$_2$(N=C^{t}Bu$_2$) (4) (0.4)	2130	15.7	2.0	none
(^{t}BuC$_5$H$_4$)TiCl$_2$(N=C^{t}Bu$_2$) (0.4)	2820	19.7	2.2	none
[Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (3) (1.0)	1190	11.9	2.1	none
Cp$_2$ZrCl$_2$ (0.02)	24300	56.3	2.4	none

[a] Cited from reference 34, conditions: ethylene, 2 atm; TEB, 5.0 mL (3.9 M); toluene, 5.0 mL (total vol., 10.0 mL); dried MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 5.0 mmol; 25 °C; 10 min. [b] Activity = kg-polymer/mol-Ti·h. [c] Estimated by GPC in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer content estimated by ^{13}C NMR spectra. [e]TBE 6.4 M.

More recently, the *tert*-BuC$_5$H$_4$ analogue (4) exhibited rather efficient TBE incorporation in the copolymerization, whereas the Cp'-ketimide analogue (2,5), constrained geometry catalyst (3), Cp$_2$ZrCl$_2$ did not incorporate TBE under the same conditions (Scheme 2.5, Table 2.4) (Khan *et al.*, 2009). The effect of both the cyclopentadienyl fragment (Cp') and the anionic donor ligands (Y) in Cp'TiX$_2$(Y) plays a crucial role for the successful copolymerization, as seen in the above copolymerization.

Scheme 2.5 (Khan *et al.*, 2009)

2.4.4 Copolymerization of ethylene with styrene by non-bridged half-titanocenes containing anionic ancillary donor ligand (Nomura, 2011)

Ethylene/styrene copolymers, which cannot be prepared by free radical or ordinary Ziegler-Natta processes (Soga et al., 1988; Mani and Burns, 1991), are promising materials due to their unique properties (Braunshweig and Breitling, 2006; Rodrigues and Carpentier, 2008; Nomura, 2010 and 2011). An introduction of styrene into polyethylene (PE) backbone results in drastic changes in both the viscoelastic behavior and thermo-mechanical properties of the polymeric material (Rodrigues and Carpentier, 2008), since the crystallizability of PE chains is gradually inhibited by the incorporation of styrene. The copolymers (ethylene-styrene inter-polymers, ESI) range from semi-crystalline to amorphous materials, depending on the styrene content (Son *et al.*, 2008). Therefore, these copolymers can become effective blend compatibilizers for blends of PE with polystyrene, and also have potential in foam, film and sheet applications.

The aryloxo modified half-titanocenes, $Cp'TiX_2(O-2,6-^iPr_2C_6H_3)$ (Cp' = cyclopentadienyl group; X = Cl, Me) exhibited high catalytic activities for ethylene/styrene copolymerization in the presence of MAO, affording poly(ethylene-*co*-styrene)s exclusively without PE and/or SPS as by-products (Antinolo *et al.*, 2000 and Itagaki, 2009). The resultant copolymers possessed not only relatively high molecular weights with unimodal molecular weight distributions, but also single composition as confirmed by DSC thermograms, CFC, and GPC/FT-IR. The activities decreased slightly with an increase in the styrene concentration, whereas the styrene contents in the copolymers increased upon increasing the [S]/[E] initial feed molar ratios. Styrene incorporations with aryloxo analogues is more efficient than that with $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**1**, X = Cl). Thus, the present catalysis provides an ef-

ficient synthesis of copolymer with high styrene content, especially higher than 50 mol%, in a random manner.