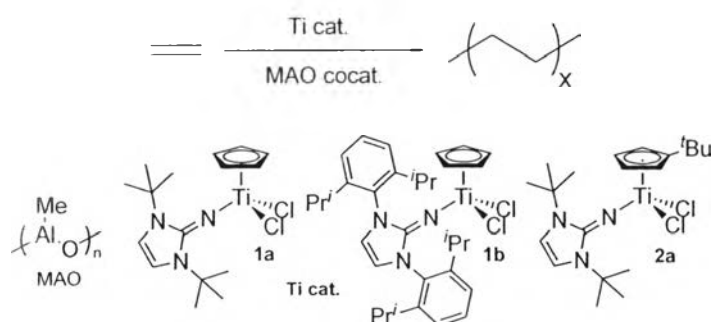# CHAPTER IV
RESULTS AND DISCUSSION

4.1 Ethylene Copolymerization by Half-Titanocenes Containing Imidazolin-2-Iminato Ligands – MAO Catlyst System

4.1.1 Ethylene polymerization using half-titanocenes containing imidazolin-2-iminato ligands – MAO catalyst systems

As shown in Scheme 1, ethylene polymerizations using half-titanocenes containing 1,3-substituted imidazolin-2-iminato ligands, Cp'TiCl$_2$[1,3-R$_2$(CHN)$_2$C=N] [Cp' = Cp (**1**), ^{t}BuC$_5$H$_4$ (**2**); R = ^{t}Bu (1,3-di-*tert*-butylimidazolin-2-imide, **a**), 2,6-^{i}Pr$_2$C$_6$H$_3$ (1,3-diisopropylphenyl-imidazolin-2-imide, **b**)], were conducted in toluene at 25 °C in the presence of MAO. MAO white solid (d-MAO), which was prepared by removing AlMe$_3$ and toluene from the commercially available samples (PMAO-S, 6.8 wt% in toluene, Tosoh Finechem Co.), was chosen in this study, because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when the Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) was used as the catalyst precursor (Nomura *et al.*, 1998). The polymerization conditions (amount of titanium charged) were optimized on the basis of polymer yields (50-180 mg). The results are summarized in Table 4.1.

Scheme 1 Ethylene polymerization using half-titanocenes containing imidazolin -2-iminato ligands – MAO catalyst systems

Table 4.1 Ethylene polymerization by $Cp'TiCl_2[1,3$-$R_2(CHN)_2C=N]$ [Cp' = Cp (1), $^tBuC_5H_4$ (2); R = ^tBu (a), 2,6-$^iPr_2C_6H_3$ (b)] - MAO catalyst systems (ethylene 6 atm, 25 °C, 10 min)

run	complex (μmol)	MAO/ mmol (Al/Ti $\times 10^{-3}$)[b]	yield/ mg	activity kg-PE/mol-Ti·h	activity kg-PE/mol-Ti·h·atm
1	1a (0.01)	0.25 (25)	79	47400	7900
2	1a (0.01)	0.50 (50)	85	51000	8500
3	1a (0.02)	1.0 (50)	86	25800	4300
4	1a (0.02)	2.0 (100)	85	25500	4250
5	1a (0.02)	3.0 (150)	83	24900	4150
6	1a (0.02)	4.0 (200)	85	25500	4250
7	1b (0.4)	1.0 (2.5)	176	2640	440
8	1b (0.4)	2.0 (5.0)	185	2780	463
9	1b (0.4)	3.0 (7.5)	93	1400	233
10	1b (0.4)	4.0 (10)	103	1550	258
11	1b (0.4)	5.0 (12.5)	101	1520	253
12	2a (0.005)	0.25 (50)	43	51600	8600
13	2a (0.005)	0.5 (100)	55	66000	11000
14	2a (0.005)	1.0 (200)	50	60000	10000
15	2a (0.02)	2.0 (100)	70	21000	3500
16	2a (0.02)	3.0 (150)	68	20400	3400

[a]Polymerization conditions: toluene + minimum quantity of CH_2Cl_2 total 30 mL, ethylene 6 atm, d-MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 10 min. [b]Molar ratio of Al/Ti.

It turned out that the activities were strongly affected by the amount of Al in the mixture rather than by the Al/Ti molar ratios (Figure 4.1). Comparing run 2 and run 3, with the same Al/Ti ratio, run 3 showed the decreasing catalytic activity due to the higher amount of Al. The similar trend was also observed in run 13 and run 15. The higher catalytic activities can be observed at the low amount of MAO in all cases, as shown in Figure 4.1. This would be probably due to that an excessive amount of MAO may deactivate the catalyst by dissociation of the anionic ligands. Among these complexes, **2a** showed the highest activities under the optimized conditions. The compared catalytic activities are in the order of 2780 kg-PE/mol-Ti·h (**1b**, run 8) < 51000 (**1a**, run 2) < 66000 (**2a**, run 13). The order is the same as that reported previously (Nomura *et al.*, 2011), and the results may suggest that an electronic factor in the *N*-substituent (and Cp') would play a role (**1a** > **1b**; **2a** > **1a**). The resultant polymers were insoluble for ordinary GPC analysis (in *o*-dichlororbenzene at 140 °C) probably due to their ultrahigh molecular weights, as reported previously (Tamm *et al.*, 2006).
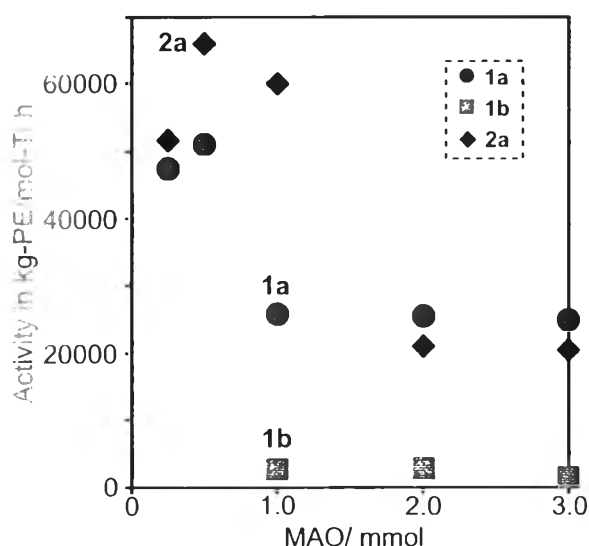

Figure 4.1 Effect of Al/Ti molar ratios on the catalytic activity in ethylene polymerization of Cp'TiCl$_2$[1,3-R$_2$(CHN)$_2$C=N] [Cp' = Cp (**1**), ^{t}BuC$_5$H$_4$ (**2**); R = ^{t}Bu (a), 2,6-^{i}Pr$_2$C$_6$H$_3$ (**b**)] - MAO catalyst systems (ethylene 6 atm in toluene, 25 °C, 10 min). Detailed data are shown in Table 4.1

Table 4.2 Selected data for ethylene polymerization by Cp'TiCl$_2$(Y) [Cp' = Cp (1), tert-Bu-C$_5$H$_4$ (2); Y = 1,3-R$_2$(CHN)$_2$C=N, R = ^{t}Bu (a), 2,6-^{i}Pr$_2$C$_6$H$_3$ (b)], or Cp' = Cp (1); Y = 1,3-R$_2$(CH$_2$N)$_2$C=N, R = ^{t}Bu (1c), Ph (1d), 2,6-Me$_2$C$_6$H$_3$ (1e)] – MAO catalyst systems.[a]

run	complex (µmol)	MAO/ mmol	activity[b]
2	CpTiCl$_2$[1,3-^{t}Bu$_2$(CHN)$_2$C=N] 1a (0.01)	0.50	51000
8	CpTiCl$_2$[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] 1b (0.4)	2.0	2780
17[c]	CpTiCl$_2$[1,3-^{t}Bu$_2$(CH$_2$N)$_2$C=N] 1c (0.05)	0.10	12720
18[c]	CpTiCl$_2$[1,3-Ph$_2$(CH$_2$N)$_2$C=N] 1d (0.1)	3.0	2580
19[c]	CpTiCl$_2$[1,3-(2,6-Me$_2$C$_6$H$_3$)$_2$(CH$_2$N)$_2$C=N] 1e (0.1)	3.0	2220
13	(tert-BuC$_5$H$_4$)TiCl$_2$[1,3-^{t}Bu$_2$(CHN)$_2$C=N] 2a (0.005)	0.50	66000

[a]Polymerization conditions: toluene + minimum quantity of CH$_2$Cl$_2$ total 30 mL, ethylene 6 atm, d-MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 10 min. [b]Activity = kg-polymer/mol-Ti·h. [c]Polymerization data by CpTiCl$_2$[1,3-R$_2$(CH$_2$N)$_2$C=N] [R = ^{t}Bu (c), Ph (d), 2,6-Me$_2$C$_6$H$_3$ (e)] (Nomura et al., 2011)

Comparing the selected polymerization results (by 1a,b,2a) under the optimized conditions with the results obtained for the Cp-1,3-imidazolidin-2-iminato analogues, CpTiCl$_2$[1,3-R$_2$(CH$_2$N)$_2$C=N] (1c-e) [R = ^{t}Bu (c), Ph (d), 2,6-Me$_2$C$_6$H$_3$ (e), Scheme 2 (Nomura et al., 2011), in Table 4.2, it turned out that 1a showed the highest catalytic activity among the Cp analogues and the activity increased in the order: 2220 (1e), 2580 (1d), 2780 (1b) < 12720 (1c) < 51000 (1a). The ligand substitution affected the activity: ^{t}Bu analogue (1a,c) showed higher catalytic activities than the phenyl analogues (1b,d,e). The fact may suggest that a stabilization of the active site by a more electron-releasing substituent is important for exhibiting high activity (Nomura et al., 1998 and 2011 and Tamm et al., 2006). Besides, it should be noted that the ^{t}BuC$_5$H$_4$ derivative (2a) showed the highest catalytic activity, probably due to a better stabilization by placing ^{t}Bu group on Cp'.
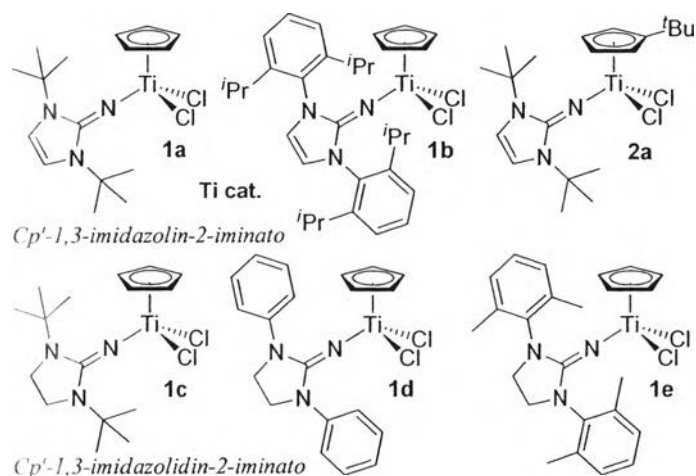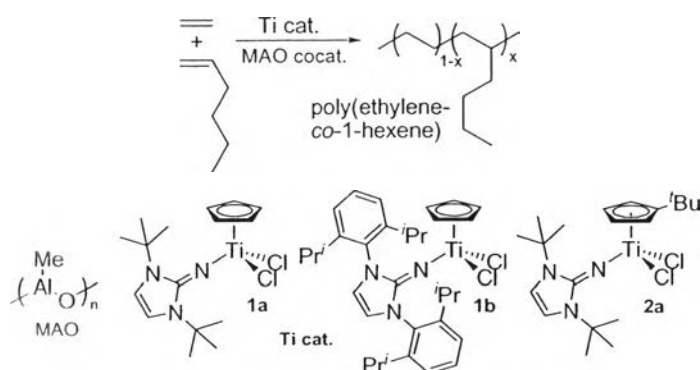
Scheme 2 Cp'-1,3-imidazolin-2-iminato (**1a**, **1b**, **2a**) and Cp'-1,3-imidazolidin-2-iminato (**1c**, **1d**, **1e**)

4.1.2 Ethylene copolymerization with α-olefins using half-titanocenes containing imidazolin-2-iminato ligands – MAO catalyst system

Copolymerizations of ethylene with 1-hexene and 1-dodecene (Scheme 2) were conducted under optimized conditions (Al/Ti molar ratios in Table 1). These copolymerizations were terminated at the initial stage, and termination with the comonomer conversion less than 10% should be very important to obtain the copolymers with uniform composition distribution and/or to evaluate the catalyst performance (r_E etc. shown below). The result obtained for $CpTiCl_2(N=C^tBu_2)$ under similar conditions (Nomura *et al.*, 2004) is also mentioned for comparison. The results are summarized in Table 4.3.

Scheme 3 Ethylene copolymerization with α-olefins using half-titanocenes containing imidazolin-2-iminato ligands – MAO catalyst system

It was revealed that $CpTiCl_2[1,3-^tBu_2(CHN)_2C=N]$, **1a**, showed the highest catalytic activity among other imidazolin-2-iminato and imidazolidin-2-iminato complexes in ethylene/1-hexene copolymerizations. The activities increased in the order: 150 kg-polymer/mol-Ti·h **(1d)** < 300 **(1e)** < 2550 **(1b)** < 4400 **(2a)**, 4620 **(1c)** < 37800 **(1a)**. These results showed an interesting contrast in ethylene homopolymerization, where **2a** showed the highest catalyst performances. The observed difference may result from both steric and electronic effect of the complex struture to the monomer coordination, as well as the coordination energy of the different monomer as revealed in ethylene/norbornene copolymerization by $CpTiCl_2(N=C^tBu_2)$ (Nomura et al., 2006). The resultant polymers especially prepared by **1a,b** and by **2a** possessed ultrahigh molecular weights with uniform molecular weight distributions (M_n = 8.8-15.7×10^5, M_w/M_n = 1.43-2.61). The activities were affected by ethylene pressure, and comonomer contents were affected by comonomer feed concetration. It was also found that **1a** and **2a** were effective in ethylene/1-dodecene copolymerizations. By use of 1-dodecene in place of 1-hexene, an increase in the activities were observed (runs 20 and 23, runs 28-31, respectively). However, 1-dodecene contents in the copolymer were low, compared to those of 1-hexene, under the similar conditions. This can be resulted from the less molar feed concentration of 1-dodecene, compared to 1-hexene, and increased steric bulk of decyl branches, compared to butyl branches, that should affect comonomer incorporations. Comparing with the Cp-ketimide analogue (run 32), **1a** showed the lower catalytic activities, and 1-hexene incorporation by **1a** was lower than that of **1c** and the Cp-ketimide analogue under the same conditions (runs 20, 25, 32).

Table 4.3 Copolymerization of ethylene with 1-hexene, 1-dodecene by Cp'TiCl₂[1,3-R₂(CHN)₂C=N] [Cp' = Cp (**1**), ^{t}BuC₅H₄ (**2**); R = ^{t}Bu (**a**), 2,6-^{i}Pr₂C₆H₃ (**b**)] - MAO catalyst systems.[a]

run	complex (μmol)	ethylene / atm	α-olefin (mL)	MAO / mmol	yield / mg	activity[b]	M_n^c ×10^{-4}	M_w/M_n^c	content[d] / mol %
20	**1a** (0.02)	6	1-hexene (5)	0.5	126	37800	131	1.51	17.0
21	**1a** (0.02)	6	1-hexene (10)	0.5	114	34200	157	1.43	29.4
22	**1a** (0.03)	4	1-hexene (10)	0.5	41	12300	107	1.82	47.6
23	**1a** (0.01)	6	1-dodecene (5)	0.5	139	83400	110	1.83	3.6
24	**1b** (0.2)	6	1-hexene (5)	2.0	85	2550	88.0	1.91	14.8
25[e]	**1c** (0.1)	6	1-hexene (5)	0.10	77	4620	94.7	1.72	28.6
26[e]	**1d** (3.0)	6	1-hexene (5)	3.0	74	150	0.116	54.0	
27[e]	**1e** (2.0)	6	1-hexene (5)	3.0	100	300	6.62	4.39	
28	**2a** (0.2)	6	1-hexene (5)	0.5	147	4400	115	2.61	6.9
29	**2a** (0.2)	6	1-hexene (10)	0.5	136	4090	82.2	2.35	13.4
30	**2a** (0.2)	6	1-dodecene (5)	0.5	204	6120	150	2.32	2.9
31	**2a** (0.2)	6	1-dodecene (10)	0.5	217	6500	124	2.41	6.6
32[f]	**Cp-Ket** (0.01)	6	1-hexene (5)	3.0	190	114000	70.4	2.40	26.9

[a]Conditions: toluene + minimum quantity of CH₂Cl₂ total 30 mL, ethylene 6 atm, d-MAO (prepared by removing toluene and AlMe₃ from ordinary MAO), 25 °C, 10 min. [b]Activity = kg-polymer/mol-Ti·h. [c]GPC data in o-dichlorobenzene vs polystyrene standards.
[d]1-Hexene content (mol %) estimated by ¹³C NMR spectra [23]. [e]Polymerization data by CpTiCl₂[1,3-R₂(CH₂N)₂C=N] [R = ^{t}Bu (**c**), Ph (**d**), 2,6-Me₂C₆H₃ (**e**)] (Nomura *et al.*, 2011). [f]Polymerization data by CpTiCl₂(N=C^{t}Bu₂) (Nomura *et al.*, 2004, 2005, 2006, 2007, 2008)

The microstructures of the resultant poly(ethylene-*co*-1-hexene)s and poly(ethylene-*co*-1-dodecene) prepared by **1a**, **2a** - MAO catalyst systems were investigated by ^{13}C NMR spectra, as shown in Figure 4.2. In all cases, resonances ascribed to two, three 1-hexene repeat units ($S_{\alpha\alpha}$, $T_{\delta\delta}$, $T_{\beta\delta}$) were observed. Although 1-hexene contents in the copolymers were close, the intensities ascribed to 1-hexene repeat/alternating sequences by **1a** and **2a** are different. This fact might support that **1a** showed better 1-hexene incorporation than **2a** (Figure 4.2a, 4.2b). Moreover, resonances ascribed to isolated 1-dodecene incorporation in addition to trace amounts of resonances ascribed to alternating and/or repeat 1-dodecene incorporation were observed in the copolymer prepared by **2a** – MAO catalyst (Figure 4.2c). This result also suggests that 1-dodecene incorporation seems more difficult than that of 1-hexene due to the steric bulk (butyl branch *vs* decyl branch, as mentioned above).
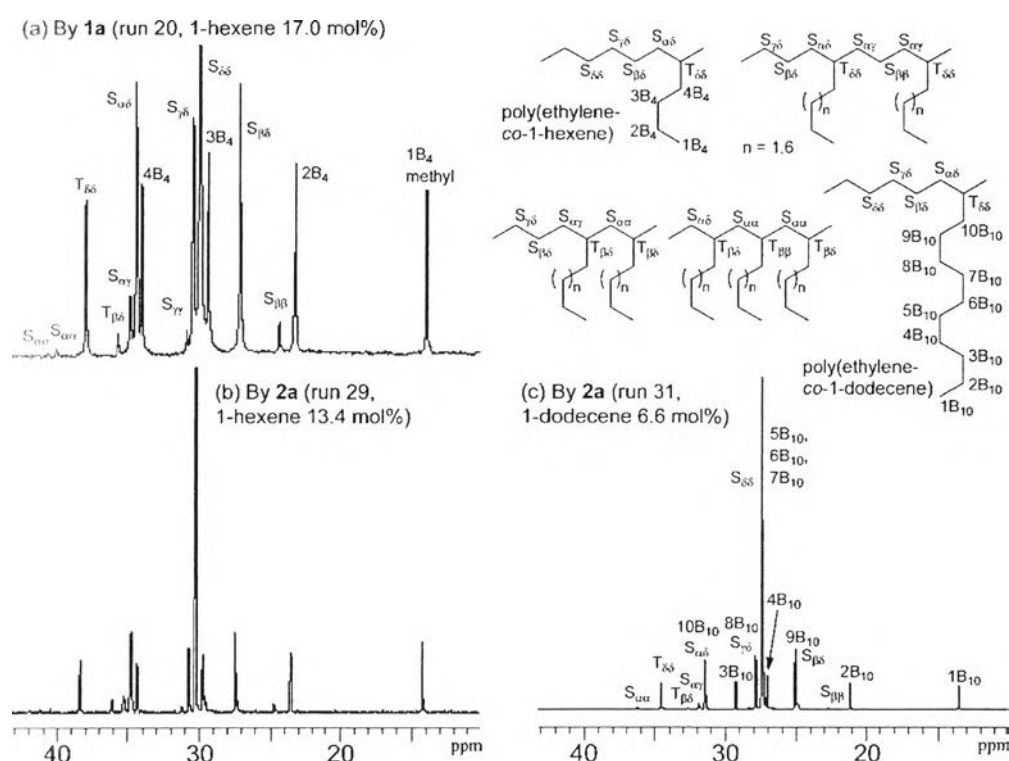

Figure 4.2 ^{13}C NMR spectra (in 1,2,4-trichlorobenzene/C_6D_6 at 120 °C) for a-b) poly(ethylene-*co*-1-hexene)s, c) poly(ethylene-*co*-1-dodecene) prepared by $Cp'TiCl_2[1,3-^tBu_2(CHN)_2C=N]$ [Cp' = Cp (**1a**), $^tBuC_5H_4$ (**2a**)] - MAO catalyst systems. Detailed polymerization data are shown in Table 4.3.

Table 4.4 summarizes triad sequence distributions, the dyads, and $r_E \cdot r_H$ values (E = ethylene, H = 1-hexene) estimated based on ^{13}C NMR spectra for poly(ethylene-co-1-hexene)s prepared by $Cp'TiCl_2[1,3-R_2(CHN)_2C=N]$ [Cp' = Cp (**1**), $^tBuC_5H_4$ (**2**); R = ^tBu (**a**), $2,6-^iPr_2C_6H_3$ (**b**)] - MAO catalyst systems (Sahgal et al., 1978; Kissin, 1985; Randall, 1989; Suhm et al., 1997 and 1998). The result obtained for $CpTiCl_2[1,3-^tBu_2(CH_2N)_2C=N]$ (**1c**) (Nomura et al., 2011), and $CpTiCl_2(N=C^tBu_2)$ (**Cp-Ket**) (Nomura et al., 2004) are also shown for comparison. The resultant $r_E \cdot r_H$ values of **1a,b,2a** ($r_E \cdot r_H$ = 0.63-0.71) were rather large compared to that of **Cp-Ket** (0.35, run 32). Although these values are somewhat lower than that of **1c** (0.94, run 31), these findings indicate that 1-hexene incorporation in the copolymerization proceeds in a random manner (1-hexene incorporations were random due to that the $r_E \cdot r_H$ values were close to 1), as observed in ordinary metallocenes and linked half-titanocenes (Suhm et al., 1997 and 1998). Moreover, the $r_E \cdot r_D$ values (E = ethylene, D = 1-dodecene) by **2a** was 0.17, indicating that the copolymerization did not proceed in a random manner due to steric bulk of the decyl branch in 1-decene (difficulty for incorporation of 1-dodecene repeatedly).

The r_E values in the ethylene/1-hexene copolymerization by **1a,b,2a** were 9.56-9.62 (**1a**), 11.8 (**1b**), 17.4 (**2a**), respectively, and the r_E values were affected by the ligand sets employed: **1a** showed better 1-hexene incorporation than **1b,2a**. These values were much larger than those obtained for **1c** (4.95, run 31), **Cp-Ket** (4.5, run 32) (Nomura et al., 2004), $[Me_2Si(C_5Me_4)(N^tBu_2)]TiCl_2$ (3.42) (Nomura et al., 2001), and $Cp^*TiCl_2(O-2,6-^iPr_2C_6H_3)$ (2.70) (Nomura et al., 2000 and 2001), but were similar to those of ordinary ansa zirconocenes [r_E = 8.2-18.9 by linked bis(indenyl)-zirconium complexes in ethylene/1-octene copolymerization] (Suhm et al., 1997). These results therefore suggest that the present catalysts show less efficient 1-hexene incorporation. It might be interesting to note that r_E values estimated for **2a** in the copolymerization between 1-hexene and 1-dodenece were close (r_E = 17.4, 18.1, respectively, runs 29-30), although the value in the ethylene/1-dodenece copolymerization was larger than those observed for the aryloxo analogue (3.71-3.95), $[Me_2Si(C_5Me_4)(N^tBu_2)]TiCl_2$ (4.26-4.31) (Kakinuki et al., 2009). The results also indicate that precise ligand modifications are important for the copolymerization

Table 4.4 Monomer sequence distributions of poly(ethylene-co-1-hexene)s, poly(ethylene-co-1-dodecene) prepared by copolymerization of ethylene with 1-hexene or 1-dodecne by Cp'TiCl$_2$[1,3-R$_2$(CHN)$_2$C=N] [Cp' = Cp (1), ^{t}BuC$_5$H$_4$ (2); R = ^{t}Bu (a), 2,6-^{i}Pr$_2$C$_6$H$_3$ (b)] - MAO catalyst systems [E: ethylene; C: 1-hexene or 1-dodecene (comonomer)].[a]

run	complex	comonomer	content[b]	triad sequence distribution[c] (%)						dyad[d]			$r_E \cdot r_C$[e]	r_E[f]	r_C[f]
			/ mol %	EEE	EEC+CEE	CEC	ECE	CCE+ECC	CCC	EE	EC+CE	CC			
20	**1a**	1-hexene	17.0	55.9	24.0	3.1	12.7	4.3	—	67.9	29.9	2.1	0.64	9.62	0.067
21	**1a**	1-hexene	29.4	36.3	26.9	7.4	17.1	12.3	—	49.7	44.1	6.2	0.63	9.56	0.066
24	**1b**	1-hexene	14.8	62.1	20.6	2.5	11.5	3.3	—	72.4	26.0	1.6	0.69	11.8	0.058
29	**2a**	1-hexene	13.4	63.4	22.7	0.5	10.5	2.2	0.62	70.9	27.3	1.8	0.71	17.4	0.041
30	**2a**	1-dodecene	6.6	73.1	20.1	0.3	6.0	0.6	—	84.4	15.5	0.1	0.17	18.1	0.009
25[g]	**1c**	1-hexene	28.6	41.4	24.4	5.6	14.8	13.8	—	53.6	39.5	6.9	0.94	4.95	0.19
32[h]	**Cp-Ket**	1-hexene	26.9	34.5	30.7	7.9	20.5	5.2	1.2	49.9	46.4	3.8	0.35	4.5	0.08

[a]For detailed polymerization conditions, see Table 3.
[b]1-Hexene or 1-dodecene content (mol %) estimated by ^{13}C NMR spectra.
[c]Estimated by ^{13}C NMR spectra
[d][EE]=[EEE]+1/2[EEC+CEE], [EC]=[CEC]+[ECE]+1/2{[EEC+CEE]+[CCE+ECC]}, [CC]=[CCC]+1/2[CCE+ECC].
[e]$r_E \cdot r_C$=4[EE][CC]/[EC+CE]^2.
[f]r_E = {[C]$_0$/[E]$_0$}×2[EE]/[EC+CE], r_C = {[E]$_0$/[C]$_0$}×2[CC]/[EC+CE], [E]$_0$ and [C]$_0$ are the initial monomer concentrations.
[g]Analysis data by CpTiCl$_2$[1,3-^{t}Bu$_2$(CH$_2$N)$_2$C=N] (**1c**) (Nomura et al., 2011).
[h]Analysis data by CpTiCl$_2$(N=C^{t}Bu$_2$) (Nomura, 2004)

to proceed with uniform catalytically active species as well as with moderate comonomer incorporation.

4.2 Efficient Ethylene/Norbornene Copolymerization by Half-titanocenec Containing Imidazolin-2-Iminato ligands – MAO catalyst system

4.2.1 Copolymerization of ethylene with norbornene (NBE) using half-titanocenes containing imidazolin-2-iminato ligands – MAO catalyst systems

Copolymerizations of ethylene with norbornene (NBE) using half-titanocenes containing 1,3-disubstituted imidazolin-2-iminato ligands, $Cp'TiCl_2[1,3-R_2(CHN)_2C=N]$ [Cp' = Cp (**1**), $^tBuC_5H_4$ (**2**); R = ^tBu (**a**), 2,6-$^iPr_2C_6H_3$ (**b**)], as shown in Scheme 4, were conducted in toluene at 25 °C in the presence of MAO. MAO white solid (d-MAO), prepared by removing $AlMe_3$ and toluene from the commercially available samples (PMAO-S, 6.8 wt% in toluene, Tosoh Finechem Co.), was chosen in this study, because it was effective in the preparation of high molecular weight ethylene/1-butene copolymers with unimodal molecular weight distributions when $Cp*TiCl_2(O-2,6-^iPr_2C_6H_3)$ was used as the catalyst precursor (Nomura *et al.*, 1998). The polymerization conditions, especially catalyst concentrations, were optimized on the basis of polymer yields (in order to control the conversions of NBE less than ca. 10-15 %). The results are summarized in Table 4.5.
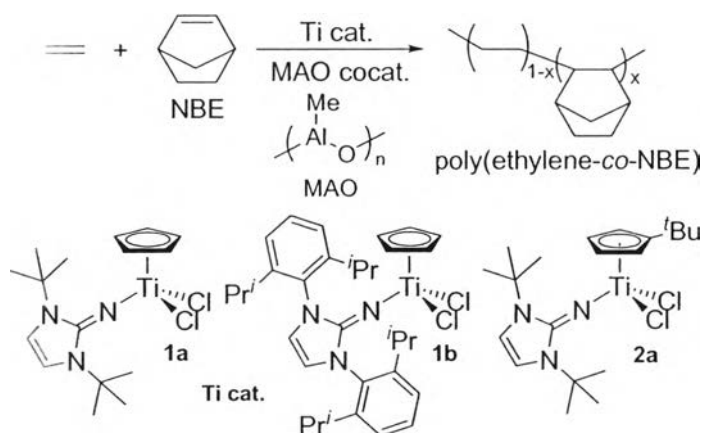
Scheme 4 Copolymerization of ethylene with norbornene (NBE) using half-titanocenes containing imidazolin-2-iminato ligands – MAO catalyst systems

Table 4.5 Copolymerization of ethylene with NBE by Cp'TiCl$_2$[1,3-R$_2$(CHN)$_2$C=N] [Cp' = Cp (1), ^{t}BuC$_5$H$_4$ (2); R = ^{t}Bu (a), 2,6-^{i}Pr$_2$C$_6$H$_3$ (b)] - MAO catalyst systems.^{a}

run	complex (μmol)	ethylene / atm	NBE^b mmol/mL	temp / °C	yield / mg	activity^c	M_n^d ×10^{-5}	M_w/M_n^d	NBE^e / mol%	T_g^f / °C
1	1a (0.10)	6	1.0	25	121	7260	16.5	2.44	27.2	76.4
2	1a (0.10)	6	2.0	25	107	6410	11.1	1.94	34.4	116.2
3	1a (0.20)	4	1.0	25	206	6180	10.8	2.53	31.4	90.6
4	1a (0.20)	4	1.0	80	192	5780	8.00	2.35	36.9	109.8
5	1a (0.40)	2	2.0	80	174	2610	0.62	1.91	53.2	217.7
6	1a (2.0)^g	--	0.5	25	115	345	0.15	2.46	100	
7	2a (1.0)	4	1.0	25	97	583	1.32	2.27	24.5	
8	1b (0.50)	4	1.0	25	46	559	14.1	7.22		
9	CGC^h (0.50)	4	1.0	25	167	2000	1.28	2.15	26.5	
10	DMSBI^h (0.10)	4	1.0	25	81	4860	2.29	2.37	29.5	
11	Ind-Phe^h (0.50)	4	1.0	25	192	2300	0.59	1.82	35.2	
12	Cp-Ket^h (0.02)	4	1.0	25	134	40200	7.19	2.92	40.7	

^{a}Conditions: toluene + minimum amount of CH$_2$Cl$_2$ total 30 mL, dried MAO (prepared by removing toluene and AlMe$_3$ from the ordinary MAO) 0.5 mmol, NBE 1.0 mmol/mL, 25°C, 10 min. ^{b}Initial norbornene (NBE) concentration charged. Activity = kg-polymer/mol-Ti·h. ^{d}GPC data in o-dichlorobenzene vs polystyrene standards. ^{e}NBE content (mol%) estimated by ^{13}C NMR spectra. ^{f}Glass transition temperature obtained from DSC measurement. ^{g}MAO 1.0 mmol. ^{h}Polymerization data by CpCl$_2$(N=C^{t}Bu$_2$) (Cp-Ket), (indenyl)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (Ind-Phe), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC) [Me$_2$Si(indenyl)$_2$]ZrCl$_2$ (DMSBI) (Nomura et $al.$, 2006).

CpTiCl$_2$[1,3-^{t}Bu$_2$(CHN)$_2$C=N] (1a) exhibited high catalytic activities in the presence of MAO. The activities were affected by ethylene pressure, temperature, as well as norbornene feed concentration. Increases in the catalytic activities were observed at higher ethylene pressure, while the activities decreased upon increasing both temperature and NBE feed concentrations under these conditions (runs 1-5). The polymerization of norbornene in the absence of ethylene also proceeded (run 6), although the activity was low. The resultant polymers

obtained from **1a** possessed high molecular weights with uniform molecular weight distributions in all cases, and single glass transition temperatures were observed in their DSC thermograms.

In contrast, (^{t}BuC$_5$H$_4$)TiCl$_2$[1,3-R$_2$(CHN)$_2$C=N] **(2a)** and CpTiCl$_2$-[1,3-(2,6-^{i}Pr$_2$C$_6$H$_3$)$_2$(CHN)$_2$C=N] **(1b)** showed the different results from those observed in ethylene/1-hexene copolymerization. The ^{t}BuC$_5$H$_4$ analogue **(2a)**, which previously showed higher catalytic activity in ethylene polymerization than **1a** (Nomura et al., 2012), which also showed moderate catalytic activity in ethylene/1-hexene copolymerization, exhibited low catalytic activity in this copolymerization. The less comonomer incorporation compared to **1a** (run 7) was observed, which is the same trend as observed in ethylene/1-hexene copolymerization. Moreover, the resulting copolymer prepared by the Cp-2,6-diisopropylphenyl analogue **(1b)** possessed broad molecular weight distribution (run 8), although **1b** showed moderate catalytic activity yielding high molecular weight copolymer with uniform composition in ethylene/1-hexene copolymerization (Nomura et al., 2012).

Comparing with the other complexes, the higher catalytic activity as well as the better NBE incorporation by **1a** (run 3) than those by [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC) and [Me$_2$Si(indenyl)$_2$]ZrCl$_2$ (DMSBI) were observed under the same conditions (runs 9-10). These results clearly indicate that **1a** is more suited as the catalyst precursor in terms of efficient synthesis of copolymers. The NBE incorporation by **1a** was similar to that by (indenyl)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (Ind-Phe) reported previously (Nomura et al., 2003), and **1a** showed higher activity under the same conditions (run 11 vs run 3). However, both the activity and the NBE contents in the copolymer by the reported Cp-ketimide analogue, CpTiCl$_2$(N=C^{t}Bu$_2$) (Cp-Ket) (Nomura et al., 2006), were higher than those by **1a**.

Table 4.6 summarizes the copolymerization results by **1a** conducted at 50 °C under low ethylene pressure and high NBE concentration conditions. The observed activity was affected by the Al/Ti molar ratio employed rather than by the initial NBE concentration charged under these conditions (runs 14-18). The higher NBE feed concentration did not result in the significant decrease in the activity (run 16 vs. run 18). The catalytic activities increased with increasing Al/Ti molar ratio.

Table 4.6 Copolymerization of ethylene with NBE by $CpTiCl_2[1,3-^tBu_2(CHN)_2C=N]$ (1a) - MAO catalyst system (ethylene 2 atm).[a]

run	1a μmol/mL	temp. /°C	NBE[b] mmol/mL	Al/ Ti[c]	yield / mg	activity[d]	M_n^e ×10^{-5}	M_w/ M_n^e	NBE[f] / mol%	T_g^g / °C
13	0.4	25	3.0	1250	102	1530	2.16	2.18	[h]	207.2
14	1.0	50	5.0	500	304	1820	1.38	1.85	55.5	230.4
15	1.0	50	5.0	1000	311	1870	1.28	1.81		
16	1.0	50	5.0	2000	337	2020	1.13	1.75		
17	1.0	50	10.0	1000	239	1430	1.05	1.85	66.5	257.6
18	1.0	50	10.0	2000	362	2170	1.10	1.83	[h]	246.5

[a]Conditions: toluene + minimum amount of CH_2Cl_2 total 10 mL, dried MAO, 10 min. [b]Initial norbornene (NBE) concentration charged. [c]Al/Ti molar ratio. [d]Activity kg-polymer/mol-Ti·h. [e]GPC data in o-dichlorobenzene vs polystyrene standards. [f]NBE content (mol%) estimated by ^{13}C NMR spectra. [g]Glass transition temperature obtained from DSC measurement. [h]NBE contents estimated from the plot of glass transition temperature vs. NBE content were 53.0 (run 13), 60.8 (run 18) mol%, respectively.
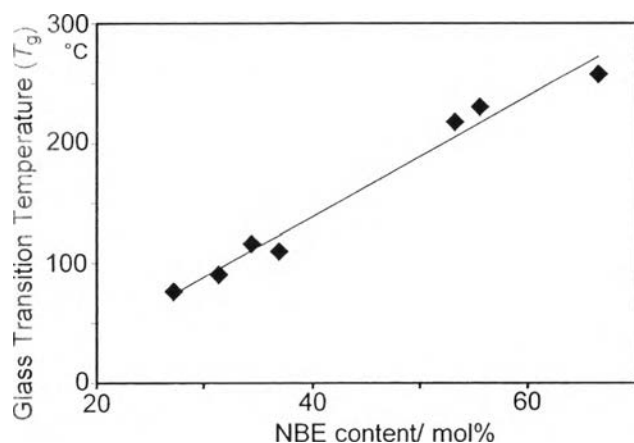

Figure 4.3 Plots of glass transition temperature vs NBE contents in poly(ethylene-co-NBE)s prepared by $CpTiCl_2[1,3-^tBu_2(CHN)_2C=N]$ (1a) - MAO catalyst system.

Note that the M_n values were not strongly affected by the NBE contents. The resultant polymers possessed high molecular weight poly(ethylene-co-NBE)s with uniform composition (confirmed by DSC thermograms) as well as molecular weight distributions. On the basis of plots of glass transition temperature (T_g) vs NBE

contents (mol%) in poly(ethylene-*co*-NBE)s prepared by **1a**, the T_g values increased linearly upon increasing the NBE contents (Figure 4.3), as demonstrated previously (Nomura, 2008). A high molecular weight poly(ethylene-*co*-NBE) with high T_g value (257.6 °C, NBE content 66.5 mol%) as well as with uniform composition (and molecular weight distribution) could be thus prepared in this catalysis.

4.2.2 Microstructure analysis for poly(ethylene-*co*-NBE)s

Figure 4.4 shows selected ^{13}C NMR spectra for the resulting poly(ethylene-*co*-NBE)s prepared by the **1a** – MAO catalyst system.   The microstructure possessed a mixture of NBE repeating units, both dyads and triads in addition to isolated and alternating NBE sequences. The spectra in figure 4.4b shows the higer intensity, compared to figure 4.4a, due to the higher NBE incorporation (66.5 mol% and 31.4 mol%, respectively).   Interestingly, the results were somewhat different from that observed by [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (CGC) and [Me$_2$Si(indenyl)$_2$]ZrCl$_2$ (DMSBI), which contained a tiny traces of NBE repeating units and both (*meso* and *racemo*) alternating ethylene-NBE sequences as well as isolated NBE units. The observed results may be suited as an appropriate explanation for the observed difference in the better NBE incorporation by **1a**, compared to CGC and DMSBI.
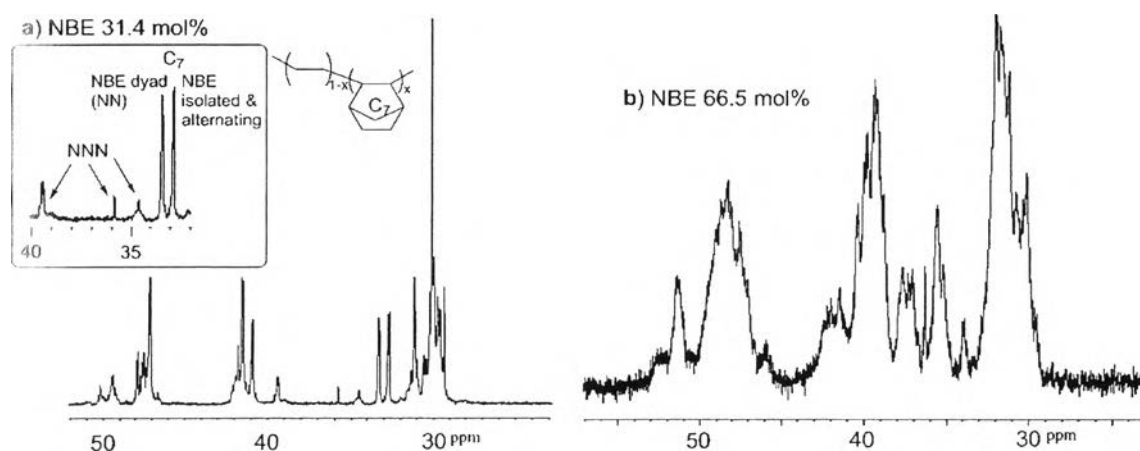

Figure 4.4 ^{13}C NMR spectra (in 1,2,4-trichlorobenzene/C$_6$D$_6$ at 120 °C) for poly(ethylene-*co*-norbornene)s prepared by CpTiCl$_2$[1,3-^{t}Bu$_2$(CHN)$_2$C=N] **(1a)** - MAO catalyst system. NBE content: 31.4 mol% (run 3), and 66.5 mol% (run 17). Detailed polymerization conditions are shown in Tables 4.5-4.6.

4.3 Efficient Terpolymerization of Ethylene and Styrene with α-Olefins by Aryloxo Modified Half-Titanocene-Based Catalysts - Cocatalyst System

In this part, terpolymerizations of ethylene, styrene with α-olefin (1-hexene, 1-decene) using aryloxo modified half-titanocenes, Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp* (1), ^{t}BuC$_5$H$_4$ (2)], in the presence of cocatalysts were conducted (Scheme 5), because these catalysts showed efficient comonomer incorporations in ethylene copolymerization with styrene as well as α-olefin. Moreover, the terpolymerization with *p*-methylstyrene (*p*-MS) in place of styrene was also explored (Scheme 6), because use of *p*-MS would be effective for the subsequent post-modifications (Chung and Dong, 2011 and Caporaso *et al.*, 2006). These studies are expected to present that the approach should be promising for synthesis of new polymers by metal catalyzed precise coordination polymerization.
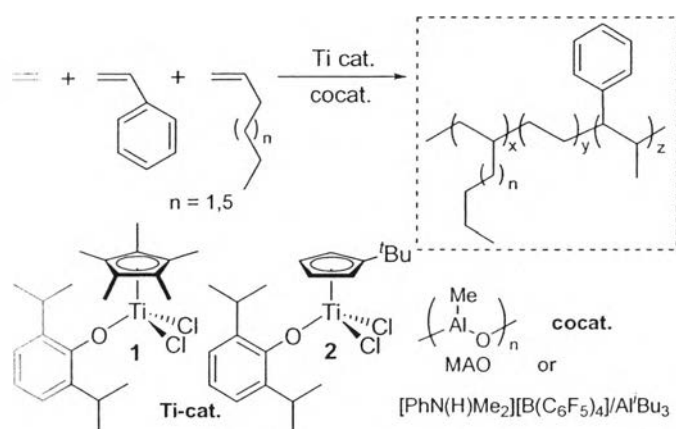
Scheme 5 Terpolymerization of ethylene, styrene with α-olefins by aryloxo modified half-titanocenes - cocatalyst system
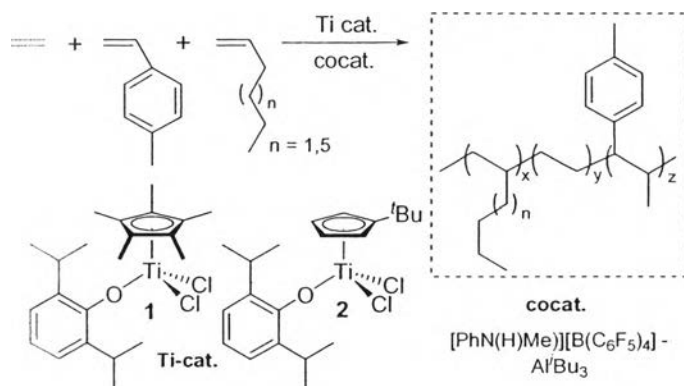
Scheme 6 Terpolymerization of ethylene, *p*-methylstyrene with α-olefins by aryloxo modified half-titanocenes - cocatalyst system

4.3.1 Terpolymerization of ethylene, styrene with α-olefins using Cp'TiCl$_2$ (O-2,6-^{i}Pr$_2$C$_6$H$_3$) – MAO systems.

In this part, terpolymerization of ethylene, styrene with α-olefins by Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**)] – MAO catalyst system was explored. MAO white solid (d-MAO), which was prepared by removing AlMe$_3$ and toluene from the commercially available samples (PMAO-S, 6.8 wt% in toluene, Tosoh Finechem Co.), was chosen, because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when **1** was used as the catalyst precursor (Nomura *et al.,* 1998). The polymerization conditions (amount of titanium charged, polymerization time etc.) were optimized on the basis of polymer yields (in order to control the conversions of comonomers less than ca. 10-15 %) (Kissin, 1985),. The results are summarized in Table 4.7 – 4.8.

In ethylene/styrene/1-hexene terpolymerization, the catalytic activities by the Cp* analogue increased with increasing 1-hexene feed concentration under certain styrene charged (runs 5-7). The increase in catalytic activities was also observed upon decreasing styrene feed concentration (runs 3-5). This is probably related to the fact that the activity generally increased upon increasing 1-hexene concentration, as observed in ethlene/1-hexene copolymerization (Nomura *et al.,* 2000^a, 2000^b and 2001). However, the results are somewhat different from that in the terpolymerization of ethylene with styrene and 1-octene by [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ – MAO system reported previously by Sernetz and Mülhaupt (1997) and Cheung *et al.* (1999), in which the activity was affected by the third comonomer (styrene) addition and the dependence was not linear under certain styrene concentration conditions.

All the resultant polymers possessed relatively high molecular weights with uniform molecular weight distributions (M_n = 4.43-5.72×10^5, M_w/M_n = 1.66-1.86, runs 3-7). 1-Hexene content increased upon increasing 1-hexene feed concentration with slightly decrease in M_n values (runs 5-7), whereas styrene content increased upon increasing styrene feed concentration (runs 3-5). it seems likely that styrene content in the copolymers was affected from 1-hexene charged under certain

Table 4.7 Terpolymerization of ethylene, styrene with 1-hexene or 1-decene by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) - MAO systems.[a]

run	Cp'	Ti / μmol	styrene / mL	[S]$_0^b$ / M	α-olefin (mL)	[C]$_0^b$ / M^b	[S]$_0$/[C]$_0$/[E]$_0^c$	yield^d / mg	aPS^e / mg	activity^f	styrene^g / mol%	α-olefin^i / mol%	M_n^j ×10^{-5}	M_w /M_n^f
1^g	Cp*	2.0	10.0	2.90	-	-	4.0/---/1.0	168	trace	504	31.9	-	0.93	1.62
2^h	Cp*	2.0	2.5	0.72	1-hexene (2.5)	0.66	1.0/0.9/---	71	2.0	36	>99	trace	0.32	2.25
3	Cp*	0.2	4.0	1.16	1-hexene (1.0)	0.27	1.6/0.4/1.0	85	28.7	2550	12.2	8.6	5.45	1.74
4	Cp*	0.2	2.5	0.72	1-hexene (2.5)	0.66	1.0/0.9/1.0	176	11.1	5290	8.8	19.7	4.74	1.66
5	Cp*	0.05	1.0	0.29	1-hexene (4.0)	1.06	0.4/1.5/1.0	106	trace	12700	2.9	28.6	4.43	1.77
6	Cp*	0.1	1.0	0.29	1-hexene (3.0)	0.80	0.4/1.1/1.0	186	7.2	11100	3.3	23.3	5.07	1.76
7	Cp*	0.1	1.0	0.29	1-hexene (2.0)	0.53	0.4/0.7/1.0	161	4.9	9660	3.4	17.5	5.72	1.86
8	Cp*	0.005	-	-	1-decene (4.0)	0.70	---/1.0/1.0	161	-	193000	-	22.3	3.30	2.50
9	Cp*	0.1	1.0	0.29	1-decene (4.0)	0.70	0.4/1.0/1.0	207	4.7	12400	4.0	20.8	5.26	1.71
10	Cp*	0.1	1.0	0.29	1-decene (3.0)	0.53	0.4/0.7/1.0	166	4.7	9950	4.9	18.7	5.36	1.80
11	Cp*	0.1	1.0	0.29	1-decene (2.0)	0.35	0.4/0.5/1.0	135	6.6	8110	5.3	13.1	6.33	1.83

[a]Polymerization conditions: total volume of toluene, 1-hexene or 1-decene, and styrene = 30 mL, ethylene 6 atm, dried MAO (prepared by removing toluene and AlMe$_3$ from the ordinary MAO) 3.0 mmol, 25 °C, 10 min. [b]Initial monomer concentration, S = styrene, C = α-olefin. [c]Initial monomer molar ratios.[32] [d]Polymer yield based on acetone insoluble fraction. [e]Atactic polystyrene (generated by MAO itself) separated as acetone soluble fraction. [f]Activity = kg-polymer/mol-Ti·h. [g]Contents estimated by ^{1}H NMR spectra.[33] [h]GPC data in o-dichlorobenzene vs polystyrene standards. [i]Cited from reference 14h. [j]Polymerization in the absence of ethylene for 1 h. [k]Nomura et al., 2012.

Table 4.8 Terpolymerization of ethylene, styrene with 1-hexene or 1-decene by $(^{t}BuC_5H_4)TiCl_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ - MAO systems.[a]

run	Cp'	Ti / μmol	styrene / mL	$[S]_0^b$ / M	α-olefin (mL)	$[C]_0^b$ / M^b	$[S]_0/[C]_0/[E]_0^c$	yield[d] / mg	aPS[e] / mg	activity[f]	styrene[g] / mol%	α-olefin[i] / mol%	M_n^j ×10⁻⁵	M_w /M_n^j
12[i]	$^{t}BuC_5H_4$	1.0	10.0	2.90	-	-	4.0/---/1.0	290	1.8	1740	50.0	-	0.24	1.60
13	$^{t}BuC_5H_4$	0.01	-	-	1-decene (4.0)	0.70	---/1.0/1.0	118	-	14100	-	23.5	2.19	2.21
14	$^{t}BuC_5H_4$	0.2	1.0	0.29	1-hexene (4.0)	0.70	0.4/1.5/1.0	375	5.1	11300	7.5	33.9	2.07	2.25
15	$^{t}BuC_5H_4$	0.2	1.0	0.29	1-decene (4.0)	0.70	0.4/1.0/1.0	251	5.2	7530	8.7	22.8	1.83	2.07
16	$^{t}BuC_5H_4$	0.1	4.0	1.16	1-decene (4.0)	0.70	1.6/1.0/1.0	389	18.4	4660	34.3	21.5	0.08	2.31

[a]Polymerization conditions: total volume of toluene, 1-hexene or 1-decene, and styrene = 30 mL, ethylene 6 atm, dried MAO (prepared by removing toluene and $AlMe_3$ from the ordinary MAO) 3.0 mmol, 25 °C, 10 min. [b]Initial monomer concentration, S = styrene, C = α-olefin. [c]Initial monomer molar ratios.[32] [d]Polymer yield based on acetone insoluble fraction. [e]Atactic polystyrene (generated by MAO itself) separated as acetone soluble fraction. [f]Activity = kg-polymer/mol-Ti·h. [g]Contents estimated by ^1H NMR spectra.[33] [h]GPC data in o-dichlorobenzene vs polystyrene standards. [i]Cited from reference 14h. [j]Polymerization in the absence of ethylene for 1 h. [k]Nomura et al., 2012.

styrene feed concentration. A slightly decrease in styrene content was observed upon increasing 1-hexene feed concentration (runs 5-7).

The same trend was also observed in ethylene/styrene/1-decene terpolymerization, whereas 1-decene was used in place of 1- hexene. The catalytic activities and 1-decene content increased with increasing 1-decene feed concentration, while styrene content and M_n values decreased (runs 9-11). The less 1-decene content in the copolymer was obtained, compared to that of 1-hexene. This was due to the less molar amount of 1-decene chareged in the system. However, it should be noted that styrene content was higher in the terpolymerization with 1-decene, compared to that of 1-hexene.

Table 4.8 showed the terpolymerization by ^{t}BuCp analogue (2). The catalytic activities were lower than those by Cp* analoge (1) under the same conditions (runs 5,9,14,15). However, the higher comonomer contents, both styrene and α-olefins, were higher. These results are in agreement with ethylene/1-hexene copolymerization as reported previously (Nomura et al., 2000 and 2001 and Khan et al., 2009). The effect of α-olefins on styrene content was also revealed as observed in the Cp* system that the styrene content slightly increased if 1-hexene was replaced with 1-dodecene under the similar conditions (runs 5,9,14,15), probably due to an increase in the initial molar ratio of styrene/α-olefin. The increase of styrene feed concentration did not affect 1-decene content in the copolymer (runs 15-16). The resultant polymers possessed relatively high molecular weights with uniform molecular weight distributions, but the M_n values were somewhat lower than those prepared by 1 under the same conditions (runs 5,9,14,15).

4.3.2 Terpolymerization of ethylene, styrene with α-olefins using Cp'TiCl$_2$ (O-2,6-^{i}Pr$_2$C$_6$H$_3$) – [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]/Al^{i}Bu$_3$ systems.

Table 4.9 summarizes results in terpolymerization of ethylene with styrene and α-olefins (1-hexene, 1-decene) using Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp* (1), ^{t}BuC$_5$H$_4$ (2)] - [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] - Al^{i}Bu$_3$ catalyst systems. Use of borate cocatalyst in place of MAO cocatalyst is believed to be effective, because it was demonstrated that the resultant polymers in the ethylene/styrene

Table 4.9 Terpolymerization of ethylene, styrene with 1-hexene or 1-decene by Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**)] – Al^{i}Bu$_3$/[PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] systems.^{a}

run	Cp'	Ti/ μmol	B/Ti^b	Al/Ti^c	styrene/ mL	α-olefin (mL)	yield/ mg	activity^d	styrene/ %^{e}	α-olefin/ %^{e}	$M_n^f \times 10^{-5}$	M_w/M_n^f
17	Cp*	0.5	1.2	500	5.0	1-hexene (5.0)	69	820	13.5	32.7	1.99	2.22
18	Cp*	0.5	1.0	500	2.5	1-hexene (2.5)	267	3200	7.8	20.8	3.55	2.30
19	Cp*	0.5	1.0	500	4.0	1-hexene (1.0)	123	1480	12.0	8.9	3.72	2.23
20	Cp*	0.2	1.2	500	1.0	1-hexene (4.0)	206	6190	2.6	28.7	4.40	2.07
21	Cp*	0.2	1.0	500	1.0	1-hexene (4.0)	87	2610	2.9	28.2	4.72	1.95
22	Cp*	0.5	1.0	1000	1.0	1-hexene (4.0)	142	1700	3.0	28.5	3.37	2.15
23	Cp*	0.5	1.0	1000	1.0	1-hexene (3.0)	116	1390	3.2	23.6	4.11	2.24
24	Cp*	0.5	1.0	1000	1.0	1-hexene (2.0)	88	1050	3.3	21.3	4.70	2.28
25	Cp*	0.5	1.0	1000	1.0	1-decene (4.0)	134	1610	3.1	24.4	3.86	2.51
26	Cp*	0.5	1.0	1000	1.0	1-decene (3.0)	111	1320	3.7	18.6	4.91	2.11
27	Cp*	0.5	1.0	1000	1.0	1-decene (2.0)	105	1260	4.0	13.7	5.37	2.40
28	^{t}BuC$_5$H$_4$	2.0	1.0	500	1.0	1-hexene (4.0)	291	872	7.5	32.9	2.97	2.34
29	^{t}BuC$_5$H$_4$	2.0	1.0	500	1.0	1-decene (4.0)	311	934	8.7	23.5	3.14	2.37

^{a}Polymerization conditions: toluene + 1-hexene or 1-decene + styrene total 30 mL, ethylene 6 atm, 25 °C, 10 min. ^{b}B/Ti molar ratio. ^{c}Al/Ti molar ratio. ^{d}Activity = kg-polymer/mol-Ti·h. ^{e}Contents estimated by ^{1}H NMR spectra.[33] ^{f}GPC data in o-dichlorobenzene vs polystyrene standards.

copolymerizations using the methyl analogue, $Cp*TiMe_2(O-2,6-{}^{i}Pr_2C_6H_3)$, were poly(ethylene-$co$-styrene)s (Zhang and Nomura, 2006): the catalyst system using the Cl analogue (1) combined with $Al(n-C_8H_{17})_3$ was also effective for exclusive preparation of the copolymers under both high styrene concentration and high temperature conditions (Nomura et $al.$, 2012[a] and 2012[b]). The catalyst system was also effective to proceed the copolymerization without by-production of atactic polystyrene produced by MAO itself (without Ti) (Zhang and Nomura, 2006; Nomura et $al.$, 2012[a] and 2012[b]).

The observed catalytic activities by 1 – $Al^{i}Bu_3/[PhN(H)Me_2]$ $[B(C_6F_5)_4]$ were lower than those by 1 – MAO system, under the same conditions [ex. 6190 kg-polymer/mol-Ti·h (run 20) vs. 12700 kg-polymer/mol-Ti·h (run 5)]. However, the comonomer contents obtained by the both system were in the same range. This indicates that cocatalyst employed has no effect on the comonomer contents, which is somewhat anologue to the previous reports in the ethylene copolymerization with 1-hexene (Nomura et $al.$, 2000 and 2001), 2-methyl-1-pentene (Nomura et $al.$, 2005 and Zhang et $al.$, 2007). The activities as well as 1-hexene and 1-decene contents increased with increasing their feed concentration, while slightly decrease in styrene and M_n valuse were observed (runs 22-24, 25-27). As previously observed in MAO system, the styrene content slightly increased if 1-hexene was replaced with 1-decene under the similar conditions. The catalytic activity was affected by aluminum-to-titanium ratio and borate-to-titanium ratio as shown in runs 20-22. The high catalytic activity can be attained at the optimized conditions. In all cases, the resultant polymers possessed relatively high molecular weights with uniform molecular weight distributions (M_n = 1.99-5.37×10^5, M_w/M_n = 1.95-2.51, runs 17-27). It should be noted that the comonomer contents can be controlled by changing comonomer charged concentration in the system. The similar trend was observed if these polymerizations by the $^{t}BuC_5H_4$ analogue (2) were conducted under the same conditions.

4.3.3 Microstructure analysis for poly(ethylene-*co*-styrene-*co*-1-hexene)s

Figure 4.5 shows a typical ^{13}C NMR spectrum and the dept spectrum for poly(ethylene-*co*-styrene-*co*-1-hexene) (in $C_2D_2Cl_4$, 110 °C). Most of resonances could be assigned on the basis of the dept spectrum and the ^{13}C NMR spectra for poly(ethylene-*co*-1-hexene)s (Nomura *et al.*, 2000 and 2001) and poly(ethylene-*co*-styrene)s (Nomura *et al.*, 2000 and 2002) prepared by these catalysts reported previously, however, assignments of some small resonances especially at 39-42 ppm (ex. marked as *) were difficult except resonances ascribed to 1-hexene repeat units (expressed as $\alpha\alpha$ in Figure 4.5). The results indicated no new resonances (or small amount) ascribed to carbons corresponding to styrene - 1-hexene insertion units.

It has been generally reported that ethylene insertion plays an important role in the preparation of copolymers consisted of propylene and styrene, and resonances ascribed to styrene – propylene (or 1-hexene) insertion units were not observed in the resultant polymers, which was due to a steric bulk where styrene and 1-hexene inserted in 2,1- and 1,2-fashion, respectively (For example Seppälä, 1985; Chien *et al.*, 1991; Arnold *et al.*, 1994; Marques *et al.*, 1995; Gerum *et al.*, 1996 and Koivumäki and Seppälä, 2008). Although it was reported that the styrene insertion in the ethylene/styrene copolymerization using **1** – MAO system was a mixture of 1,2- and 2,1- insertion units and resonances denoted as $S_{\alpha\beta}$ (Figure 4.5) were observed in the ^{13}C NMR spectra (Nomura *et al.*, 2000 and 2002), as described above, the resonances ascribed to styrene – 1-hexene repeat units were negligible (or observed in small amount). So, a possibility that the reultant polymers are a mixture of two copolymers (ethylene/styrene copolymer and ethylene/1-hexene copolymer) or block copolymer consisting of ethylene/styrene block and ethylene/1-hexene block are considered. However, the DSC analysis showed no melting temperature even with low styrene contents, although the poly(ethylene-*co*-styrene)s with low styrene contents (ex. 4.0 mol% in run 9: 5.3 mol% in run 11) generally possess melting temperatures (Semetz and Mülhaupt, 1997; Cheung et al., 1999; Braunschweig and Breitling, 2006; Rodrigues and Carpentier, 2008; Nomura, 2010 and 2011). The results thus strongly suggest that the resultant polymers are terpolymers (amorphous materials) with uniform compositions.
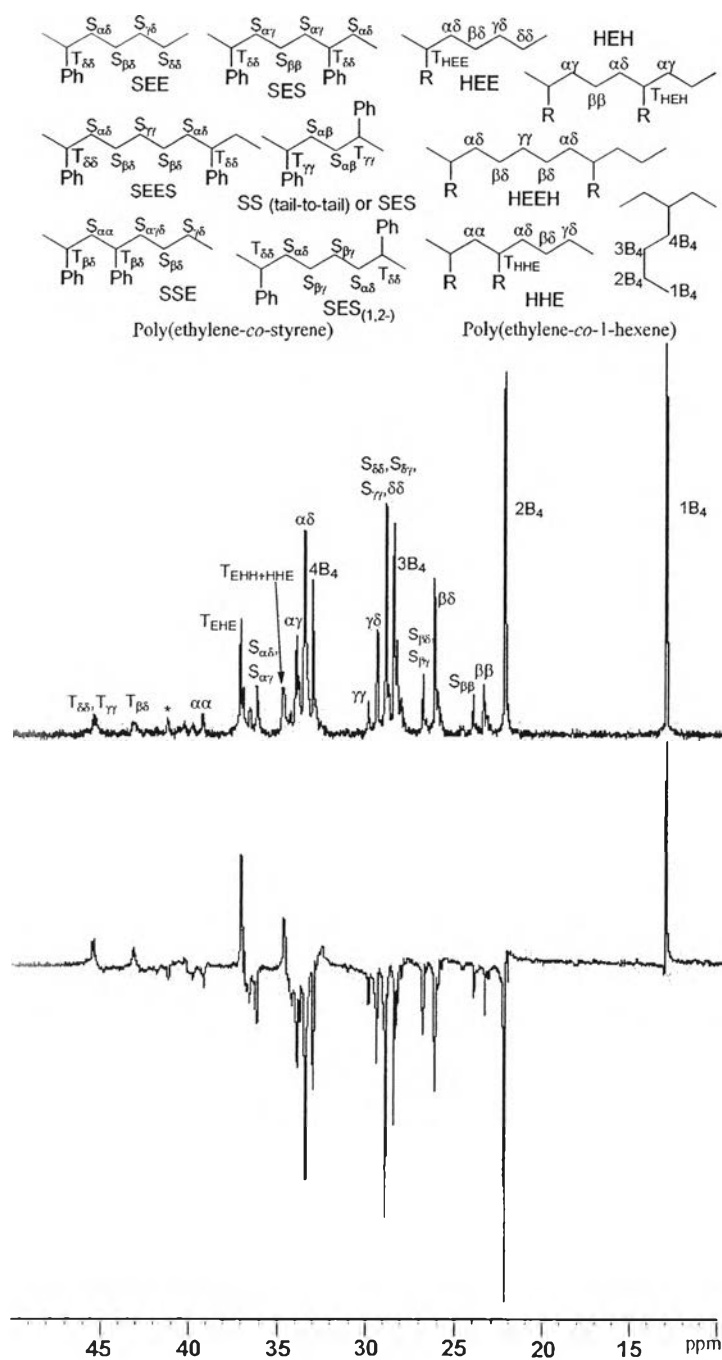
Figure 4.5 ^{13}C NMR spectrum (top) and the dept (bottom) spectrum for poly(ethylene-*co*-styrene-*co*-1-hexene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (sample run 17, Table 4.9).

4.3.4 Terpolymerization of ethylene, *p*-methylstyrene (*p*-MS) with α-olefins using Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) – [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$]/Al^{i}Bu$_3$ systems.

In this part, *p*-methylstyrene was used in place of styrene in the terpolymerization in the presence of [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] - Al^{i}Bu$_3$ as cocatalyst, because use of MAO generated large amount of atactic poly(p-MS) as by products under these conditions. Introduction of *p*-MS should be effective for the subsequent post-modifications (to introduce additional functionality), because it has been known that the methyl group in *p*-MS can be used as the initiating fragment for anionic polymerization after treatment with *s*-BuLi (Chung and Dong, 2001; Caporaso *et al.,* 2006). The terpolymerization reults of ethylene, *p*-MS with α-olefins using Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**)] – Al^{i}Bu$_3$/[PhN(H)Me$_2$] [B(C$_6$F$_5$)$_4$] systems are summarized in Table 4.10.

Table 4.10 Terpolymerization of ethylene, p-methylstyrene (p-MS) with 1-hexene or 1-decene by $Cp'TiCl_2(O-2,6-{}^iPr_2C_6H_3)$ [Cp' = Cp^* (1), ${}^tBuC_5H_4$ (2)] – $Al^iBu_3/[PhN(H)Me_2][B(C_6F_5)_4]$ systems.[a]

run	Cp'	Ti / μmol	p-MS / mL	α-olefin (mL)	yield / mg	activity[b]	p-MS / %[c]	α-olefin[c] / %	M_n[d] × 10^{-5}	M_w/M_n[d]
30	Cp^*	0.5	2.5	1-hexene (2.5)	75	905	18.5	20.1	4.58	1.34
31	Cp^*	1.0	1.0	1-hexene (4.0)	174	1050	4.6	26.7	2.16	2.25
32	Cp^*	1.0	1.0	1-hexene (3.0)	164	980	5.8	24.1	2.50	2.06
33	Cp^*	1.0	1.0	1-hexene (2.0)	135	810	6.1	18.7	2.70	2.28
34	Cp^*	1.0	1.0	1-decene (4.0)	154	924	4.6	21.0	2.27	2.07
35	Cp^*	1.0	1.0	1-decene (3.0)	119	715	5.0	16.4	2.57	2.21
36	Cp^*	1.0	1.0	1-decene (2.0)	101	606	6.1	13.3	2.70	2.29
37	${}^tBuC_5H_4$	2.0	1.0	1-hexene (4.0)	219	649	8.4	33.8	3.38	2.53
38	${}^tBuC_5H_4$	2.0	1.0	1-decene (4.0)	191	573	8.8	19.6	3.48	2.42

[a]Polymerization conditions: toluene + 1-hexene or 1-decene + p-methylstyrene total 30 mL, ethylene 6 atm, B/Ti molar ratio = 1, Al/Ti molar ratio = 500, 25 °C, 10 min. [b]Activity = kg-polymer/mol-Ti·h. [c]Contents estimated by ${}^1H$ NMR spectra.[33] [d]GPC data in o-dichlorobenzene vs polystyrene standards.

The resultant polymers by **1** and **2** possessed relatively high molecular weights with unimodal molecular weight distributions (M_n = 2.16-4.58×10^5, M_w/M_n = 1.34-2.29). The catalytic activity by Cp* analogue (**1**) increased with increasing α-olefin feed concentration, as observed in the previous parts. However, p-MS contents in the copolymer was higher than styrene contents under the similar conditions. Although it was found in ethylene/styrene/α-olefin terpolymerization that styrene contents in the system with 1-decene were slightly higher than those with 1-hexene under the same conditions, in the terpolymerization whereas p-MS was used in place of styrene, the similar trend was not observed. Compared to **1**, 'BuCp analogue (**2**) showed the lower catalytic activity but higher comonomer contents, as previously observed in ethylene/styrene/α-olefin terpolymerization.

Figure 4.6 shows a typical ^{13}C NMR spectrum in the resultant polymer. Most of resonances could be assigned on the basis of the spectrum shown in Figure 5.1, and resonance ascribed to carbon in the methyl group in p-MS was observed at ca. 20.3 ppm. Assignments of some small resonances especially at 39-42 ppm were difficult. As demonstrated in the terpolymer of poly(ethyene-co-styrene-co-1-hexene), in Figure 4.5, the resultant polymer does not possess resonances ascribed to 1-hexene - p-MS repeat units. The result suggests that the resultant polymer possesses similar microstructure to poly(ethylene-co-styrene-co-1-hexene).
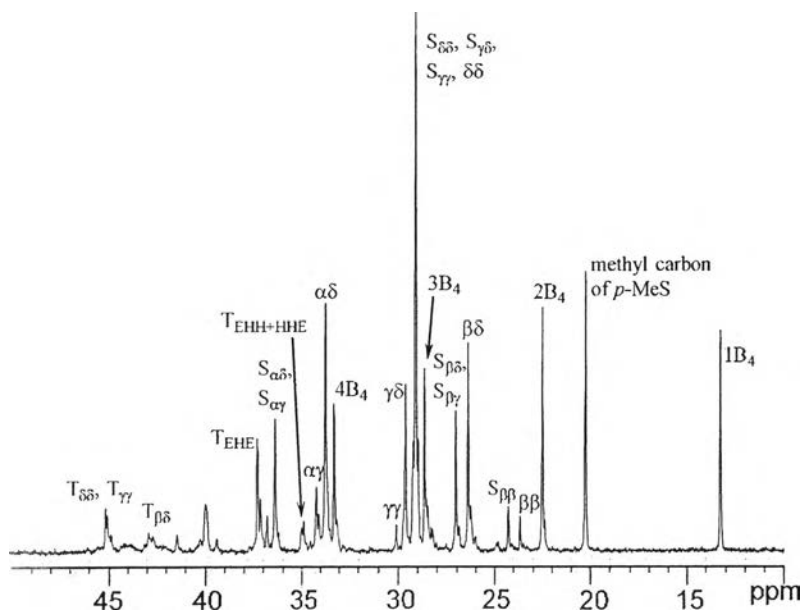
Figure 4.6 ^{13}C NMR spectrum for poly(ethylene-*co-p*-methylstyrene-*co*-1-hexene) in 1,1,2,2-tetrachloroethane-d_2 at 110 °C (sample run 31, Table 4.10).

4.4 Introduction of Reactive Functionality by Incorporation of Divinylbiphenyl in Ethylene Copolymerization with Styrene or 1-Hexene Using Aryloxo-Modified Half-Titanocenes – MAO Catalysts

4.4.1 Copolymerization of ethylene with styrene or 1-hexene using Cp'TiCl$_2$(OAr) – MAO catalysts in the presence of 3,3'-divinyldiphenyl.
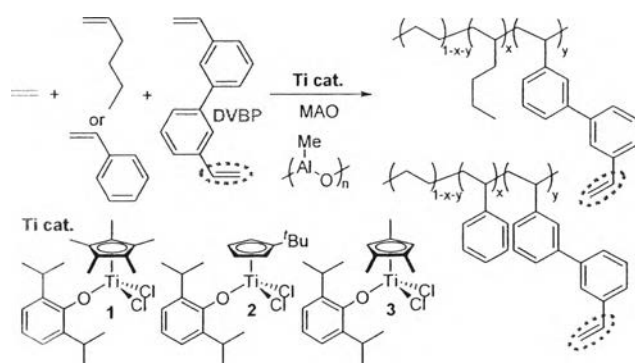
Scheme 7 Copolymerization of ethylene with styrene or 1-hexene using Cp'TiCl$_2$(OAr) – MAO catalysts in the presence of 3,3'-divinyldiphenyl

In this part, half-titanocenes containing aryloxo ligand, Cp'TiCl$_2$ (OAr) [Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**), 1,2,4-Me$_3$C$_5$H$_2$ (**3**); Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ was used as the catalyst precursors for this study, because this type of complex showed highly efficient comonomer, styrene (Nomura *et al.*, 1998, 2000 and Kakinuki, 2009) and α-olefins (Nomura, 2000, 2002 and 2012), incorporation in the ethylene copolymerization and an efficient repeated insertion of 1,7-octadiene (OD) without cyclization affording unsaturated polymers could be attained in the OD polymerization and ethylene/1-octene/OD terpolymerization using **1** – MAO catalyst (Dassaud *et al.*, 1993; Uozumi *et al.*, 2000; Arnold *et al.*, 2002; Mathers and Coates, 2004; Nomura *et al.*, 2007 and Nomura, 2010). MAO white solid (d-MAO), prepared by removing AlMe$_3$ and toluene from the commercially available samples (PMAO-S, 6.8 wt% in toluene, Tosoh Finechem Co.), was chosen as the cocatalyst, because it was effective in the preparation of high molecular weight ethylene/α-olefin copolymers with unimodal molecular weight distributions when **1** was used as the catalyst precursor (Nomura *et al.*, 1998). These polymerizations were terminated at the initial stage on the basis of polymer yields in order to control the conversions of each comonomers less than ca. 10-15 %. The results are summarized in Table 4.11.

(1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**) showed the highest catalytic activities in ethylene copolymerization with styrene and 3,3-divinylbiphenyl (DVBP). The compared activites were ^{t}BuC$_5$H$_4$ analogue (1100), Cp* (1230) < Me$_3$C$_5$H$_2$ (3100) upon similar conditions. The activities were affected by ethylene pressure and ratio of initial monomer feed concentration. The increase in catalytic activity was observed upon increasing ethylene pressure. The polymers prepared by **3** possessed high molecular weight with unimodal molecular weight distribution. It also turned out that the activities, the styrene contents, and the molecular weight of these polymers (runs 1-6) were relatively close to those observed in ethylene/styrene copolymerization [ex. activity 1600 kg-polymer/ mol-Ti·h, M_n = 7.45x10^4, styrene 38.2 mol% + DVBP 4.1 mol% (run 2); activity 1100 kg-polymer/mol-Ti·h, M_n = 6.0x10^4, styrene 41.1 mol% (run 19, cited from Nomura *et al.*, 2002)]. The comonomer contents can be controlled by comonomer feed concentration. The higher DVBP content in the copolymer can be attained at higher DVBP charged, however, no significant decreases in both the activities and M_n values were observed

Table 4.11 Terpolymerization of ethylene (E) with styrene or 1-hexene and 3,3'-divinylbiphenyl (DVBP) by Cp'TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp' = Cp* (1), ^{t}BuC$_5$H$_4$ (2), 1,2,4-Me$_3$C$_5$H$_2$ (3)] - MAO catalysts.[a]

run	Ti cat. (μmol)	E (atm)	comonomer (mL)	DVBP (mL)	yield[b] (mg)	activity[c]	DVBP (mol%)[d]	comonomer (mol%)[d]	Mn[e] x10-4	Mw/ Mn[e]
1	1,2,4-Me$_3$C$_5$H$_2$(1.0)	6	styrene (5.0)	0.5	451	2700	3.3	27.4	16.3	2.63
2	1,2,4-Me$_3$C$_5$H$_2$(1.0)	4	styrene (5.0)	0.5	260	1600	4.1	38.2	7.45	2.00
3	1,2,4-Me$_3$C$_5$H$_2$ (0.5)	6	styrene (5.0)	0.5	258	3100	3.2	30.3	23.1	2.61
4	1,2,4-Me$_3$C$_5$H$_2$ (0.5)	4	styrene (5.0)	0.5	97.6	1200	4.0	39.0	6.57	1.83
5	1,2,4-Me$_3$C$_5$H$_2$ (1.0)	4	styrene (5.0)	1.0	140	840	6.5	35.9	5.81	1.90
6	1,2,4-Me$_3$C$_5$H$_2$ (1.0)	4	styrene (5.0)	1.0	164	990	6.4	35.5	6.24	2.17
7	tBuC$_5$H$_4$(1.0)	6	styrene (5.0)	0.5	184	1100	3.1	28.5	2.22	2.55
8	tBuC$_5$H$_4$(1.0)	4	styrene (5.0)	0.5	66.7	400	3.4	38.4	1.49	2.49
9	tBuC$_5$H$_4$ (0.5)	6	1-hexene (5.0)	0.5	275	3310	3.3	48.8	10.7	2.22
10	Cp* (1.0)	6	styrene (5.0)	0.5	205	1230	2.2	23.2	5.50	2.11
11	Cp* (0.05)	6	1-hexene (5.0)	0.5	140	16800	1.7	33.9	39.7	2.57
12	Cp* (0.05)	4	1-hexene (5.0)	0.5	115	13800	2.1	35.1	31.6	2.54

[a] Conditions: toluene+styrene or 1-hexene+3,3'-divinylbiphenyl total 30 mL, dried MAO (prepared by removing toluene and AlMe$_3$ from the ordinary MAO) 3.0 mmol, 25 °C, 10 min. [b] Isolated polymer yield as acetone insoluble fraction, and yield of atactic polystyrene, prepared by MAO itself, was obtained as acetone soluble fraction. [c] Activity = kg-polymer/mol-Ti·h. [d] Contents estimated by ^{1}H NMR spectra. [e] GPC data in o-dichlorobenzene vs polystyrene standards.

(runs 2,4-6). Both styrene and DVBP contents in the copolymers by **3** were similar to those by **2**, as expected from the results in the ethylene/styrene copolymerization (Nomura *et al.,* 2002). All the resultant polymers were highly soluble for measurement of molecular weights and their distributions in the standard GPC analysis (in *o*-dichlorobenzene at 140 °C), indicated to the efficient copolymerization without cross-linking.

Although Cp* analogue (**1**) showed the low catalytic activity in ethylene copolymerization with styrene in the presence of DVBP, the copolymerization of ethylene with 1-hexene in the presence of DVBP by **1** proceeded with remarkable catalytic activities, as expected from the previous report (Nomura *et al.,* 1998 and 200; Kakinuki *et al.,* 2009), affording high molecular weight polymers with unimodal molecular weight distributions (runs 11,12). The catalytic activity was affected by ethylene pressure. Although the activity by $^{t}BuC_5H_4$ analogue (**2**) was lower than **1**, more efficient 1-hexene and DVBP incorporation can be attained by **2** (run 9 *vs* run 11).

4.4.2 NMR spectra of poly(ethylene-co-styrene-co-DVBP)s.

Figure 4.7 shows a typical ^{13}C NMR spectrum in the resultant polymer prepared by the 1,2,4-Me$_3$C$_5$H$_2$ (**3**) analogue – MAO catalyst (run 5). Most of resonances could be assigned on the basis of poly(ethylene-*co*-styrene)s reported previously (Nomura *et al.,* 2000 and 2002). In addition to the resonances at $\delta = 34.3$ and 35.1 ppm, which are attributed to $S_{\alpha\beta}$ (tail-to-tail coupling of styrene unit or head-to-head bridged by an intervening ethylene unit, SES), the resonances at $\delta = 40.7$-41.0 ppm ($T_{\beta\beta}$, three styrene unit connected to head-to-tail coupling) and 43.1-45 ppm ($S_{\alpha\alpha}$ and $T_{\beta\delta}$, two styrene unit connected to head-to-tail coupling) were observed. Moreover, two resonances ascribed to the vinyl carbon were observed at 113.4 and 136.4 ppm, and resonances ascribed to carbon in the biphenyl moiety as well as carbon attached to the vinyl group would be observed (probably ca. 137.5, and 140-141 ppm marked as + in Figure 1). These results suggest that (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) exhibits an efficient styrene and DVBP incorporation, affording copolymer even with styrene content.

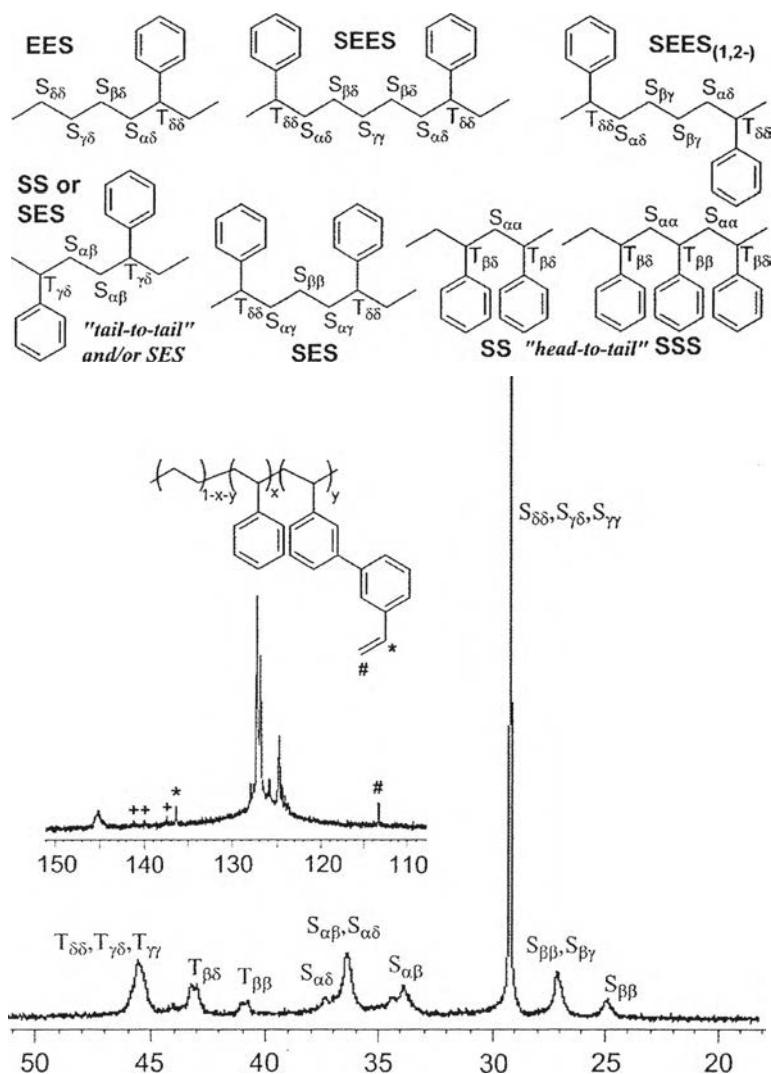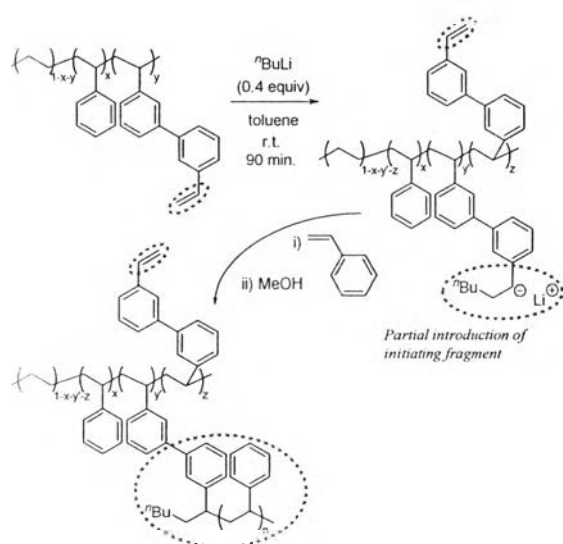**Figure 4.7** ^{13}C NMR spectrum for poly(ethylene-*co*-styrene-*co*-3,3-divinylbiphenyl) prepared by (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (3) - MAO catalyst. (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C, run 5 in Table 4.11).

4.4.3 Post (grafting) polymerization of styrene.

The resultant polymer (run 5, Table 4.11) was treated with n-BuLi in toluene at roomtemperature and styrene polymeriation was started by addition of styrene in the reaction mixture (Scheme 7). The resulting polymer after the post polymerization showed the increase in both the M_n value and yield compared to the starting polymer [$M_n = 8.67 \times 10^4$ vs. 5.81×10^4 (run 5)] and possessed unimodal molecular weight distribution ($M_w/M_n = 2.42$). The amount of atactic polystyrene

extracted as the acetone soluble fraction was negligible. From ^{13}C NMR spectra (Figure 4.8), an increase of intensity in the resonances especially ascribed to carbon of (more than) three styrene repeat units ($T_{\beta\beta}$) in the ^{13}C NMR spectrum was observed, which is in agreement with higher styrene content (50.6 mol%), compared to the starting material with 35.9 mol% styrene. However, since the vinyl groups were partially initiated by n-BuLi, some vinyl groups were still remained in the resultant polymer.

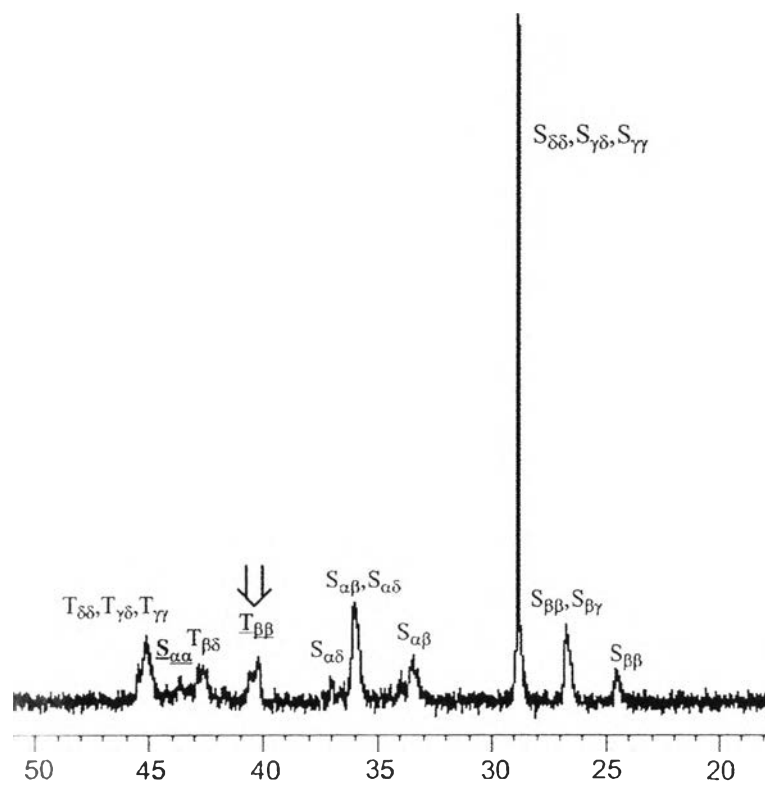**Scheme 8** Post (grafting) polymerization of styrene

Figure 4.8 ^{13}C NMR spectrum for poly{(ethylene-*co*-styrene-*co*-3,3-divinyl biphenyl)-*graft*-styrene} (in 1,1,2,2-tetrachloroethane-d_2 at 110 °C).