Synthesis and polymerization behavior of various substituted indenyl titanium complexes as catalysts for syndiotactic polystyrene

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Abstract

Five substituted indenyltrichlorotitanium compounds have been synthesized and characterized by spectroscopic methods and their catalytic behavior for the polymerization of styrene was studied in the presence of methylaluminoxane (MAO) as a cocatalyst. Substituted indenyl ligands include 1,3-dimethyl, 1-methyl, 1-ethyl, 1-isopropyl and 1-(trimethylsilyl)indenyl groups. All five compounds gave extremely pure syndiotactic polystyrene, with conversion rates of at least 95%, and their catalytic properties were compared with the data obtained from the (η^5-indenyl)trichlorotitanium–MAO system. The catalytic activity is enhanced by less bulky and better electron-releasing substituents of the indenyl ligand.

Keywords: Titanium metallocene; Indenyl derivatives; Catalysts; Syndiotactic polystyrene

1. Introduction

Since the discovery of the Ziegler–Natta catalyst systems in the early 1950s, the metallocene complexes of Group 4 metals have become an important class of homogeneous catalysts for the synthesis of polymers and organic compounds [1]. In particular, the use of the $TiCl_4$–methylaluminoxane (MAO) system in the first preparation of syndiotactic-polystyrene (sPS) by Ishihara and coworkers has spurred an active search for new types of sPS catalysts, leading to the observation that titanium compounds of the type (η^5-Cp')TiX$_3$ (Cp' = cyclopentadienyl ligand or its derivative; X = halide, alkoxides or alkyl groups) are among the most effective sPS catalysts [2].

In 1993, Rausch and coworkers reported the first sPS catalyst containing indenyl ligand and found that the (η^5-indenyl)TiCl$_3$–MAO system catalyzed the polymerization of styrene over a wide range of polymerization temperature more effectively than CpTiCl$_3$–MAO [3]. The catalytic behavior of (η^5-indenyl)TiCl$_3$ has been attributed to the greater electron-donating ability

of the indenyl ring relative to the Cp ligand [4]. In general, basicity, steric effects and chirality of the ligands attached to the Group 4 metal centers strongly influence the polymerization. Nonetheless, the effect of the substituents in the indenyl ligand of (η^5-indenyl)TiCl$_3$ on the styrene polymerization is not been properly reported [5]. We synthesized various substituted indenyltrichlorotitanium complexes with different electronic and steric factors and explored their catalytic behavior in the formation of sPS in the presence of MAO as a cocatalyst. Reported herein are accounts of the synthesis, characterization and catalytic properties of (η^5-L)TiCl$_3$ (L = 1,3-dimethyl, 1-methyl, 1-ethyl, 1-isopropyl and 1-(trimethylsilyl)indenyl ligands) in sPS formation.

2. Experimental section

All operations were performed under pure dinitrogen atmosphere using a Vacuum Atmosphere drybox equipped with a Model HE 493 Dri-Train gas purifier or standard Schlenk techniques [6]. Dinitrogen was deoxygenated with activated Cu catalyst and dried with drierite. n-Hexane, benzene, and toluene were distilled under dinitrogen from sodium–potassium alloy and

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stored over the activated molecular sieves 3A [7]. Dichloromethane was distilled under dinitrogen from CaH_2 [7]. ^1H and $^{13}C\{^1H\}$ FT-NMR spectra were recorded on a Bruker AC200 or AM300 spectrometer. ^{29}Si NMR and $^{47,49}Ti$ NMR spectra were obtained on a Bruker AM300 spectrometer with a 10 mm diameter broad-band probe at 323 K. Melting points were determined using an Electrothermal Model 1307 digital analyzer. FT-IR spectra were measured using a Bomem Michelson Series FT-IR spectrophotometer, and UV–visible spectra were obtained with a Shimadzu UV-3100S. GPC data of selected sPS samples were measured at Samsung Chemical Technology Center. Electron impact mass spectra were obtained by Korea Basic Science Center, Taejon, South Korea. Elemental analyses were performed by the Oneida Research Services, Inc., Whitesboro, NY.

2.1. Synthesis

The compounds (1-trimethylsilyl)-1,3-dimethylindene, (1-trimethylsilyl)-1-methylindene, 1,1- or 1,3-bis(trimethylsilyl)indene, 3-ethylindene, 3-isopropylindene and (η^5-indenyl)trichlorotitanium were prepared by modified literature procedures [8]. $TiCl_4$ (1 M solution in toluene), chlorotrimethylsilane (98%), ^nBuLi (1.6 M solution in hexane) and styrene monomer were obtained from Aldrich Chemical Co. Solid MAO (Me/Al = 1.63, Al = 15.682 mmol g^{-1}) was received as a gift from an industrial company in Korea.

2.2. (η^5-1,3-Dimethylindenyl)trichlorotitanium (1)

A solution of (1-trimethylsilyl)-1,3-dimethylindene (1.95 g, 9 mmol) in 20 ml of CH_2Cl_2 was added dropwise to a solution of $TiCl_4$ (9.9 ml, 9.9 mmol) in 20 ml of CH_2Cl_2 at room temperature. The resulting reaction mixture was stirred for 24 h and filtered. The volume of the filtrate was reduced by two-thirds and then hexane was added. Storage of the resulting solution at $-20\,°C$ for 24 h resulted in the formation of dark red solid which was collected by decantation, washed with n-hexane twice and dried in vacuo. The product was obtained in a yield of 75% (2.0 g). M.p. 139–141 °C. ^1H NMR (CDCl₃, 300.13 MHz): δ 7.76–7.51 (m, 4H), 6.81 (s, 1H), 2.76 (s, 6H). $^{13}C\{^1H\}$ NMR (CDCl₃, 75.1 MHz): δ 132.8, 131.2, 129.0, 125.7, 123.9, 16.04. IR (Nujol mull) cm^{-1}: 755 s, 889 s, 1022 m, 1136 w, 1170 w, 1220 m, 1532 w, 1605 m, 3100 w. UV (benzene) λ_{max} (ε, 1cm^{-1} mol^{-1}): 403 nm (2000), 561 nm (1050). MS (m/e, % intensity): 296 (4, M$^+$), 261 (4, M − Cl$^+$), 225 (5, M − 2Cl$^+$), 143 (100, M − 3Cl − Ti$^+$), 128 (55, M − 3Cl − Ti − CH₃$^+$), 115 (26, indene$^+$). Anal. Found: C, 44.91; H, 3.67. $C_{11}H_{11}Cl_3T$. Calc.: C, 44.42; H, 3.73%.

2.3. (η^5-1-Methylindenyl)trichlorotitanium (2)

A dark red solid 2 was prepared in a yield of 83% (2.35 g) by reacting (1-trimethylsilyl)-3-methylindene (1.30 g, 10 mmol) with $TiCl_4$ (11 ml, 11 mmol) in a manner analogous to the procedure for 1. M.p. 104–105 °C. ^1H NMR (CDCl₃, 200.13 MHz): δ 7.79 (d, $J = 1.73$ Hz, 1H), 7.75 (d, $J = 1.73$ Hz, 1H), 7.52 (m, 2H), 7.13 (d, $J = 3.30$ Hz, 1H), 6.93 (d, $J = 3.31$ Hz, 1H), 2.76 (s, 1H). $^{13}C\{^1H\}$ NMR (CDCl₃, 50.32 MHz): δ 133.5, 131.3, 130.9, 129.6, 129.5, 127.6, 125.3, 123.5, 115.8, 15.66. IR (Nujol mull) cm^{-1}: 752 s, 833 s, 913 w, 997 w, 1033 m, 1216 m, 1298 w, 1534 m, 1561 w, 1606 w, 1674 w, 1811 w, 3094 w. UV (benzene) λ_{max} (ε, 1cm^{-1} mol^{-1}): 398 nm (2100), 538 nm (1200). MS (m/e, % intensity): 282 (96, M$^+$), 247 (36, M − Cl$^+$), 211 (100, M − 2Cl$^+$), 126 (65, M − 3Cl − Ti$^+$), 115 (33, indene$^+$). Anal. Found: C, 42.84; H, 3.16. $C_{10}H_9Cl_3Ti$. Calc.: C, 42.38; H, 3.20%.

2.4. (1-Trimethylsilyl)-3-ethylindene

^nBuLi (10.3 ml, 16.5 mmol) was added dropwise to a stirred, cold (0 °C) solution of 3-ethylindene (2.16 g, 15 mmol) in 50 ml of n-hexane. The reaction mixture was allowed to warm to room temperature and stirred for 12 h before filtration. The solvent was removed under vacuum and 50 ml of benzene was added. Subsequently, neat chlorotrimethylsilane (2.14 ml, 16.5 mmol) was added dropwise via a syringe. The yellow solution was allowed to warm to 80 °C and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was redissolved in dichloromethane and the resulting mixture was filtered through a Celite bed. The removal of solvent from the filtrate gave yellow oil (2.27 g, 70.1%). ^1H NMR (CDCl₃, 200.13 MHz): δ 7.47–7.15 (m, 4H), 6.32 (d, $J = 1.36$ Hz, 1H), 3.40 (d, $J = 1.89$ Hz, 1H), 2.65 (m, 2H), 1.32 (t, $J_{1,2} = J_{3,2}$ = 7.46 Hz, 3H), −0.03 (m, 9H). $^{13}C\{^1H\}$ NMR (CDCl₃, 50.32 MHz): δ 146.2, 144.4, 143.5, 128.7, 124.4, 123.5, 122.8, 118.7, 44.36, 20.78, 13.14, −2.509.

2.5. (η^5-1-Ethylindenyl)trichlorotitanium (3)

A dark red solid 3 was prepared in a yield of 81% (2.38 g) by reacting (1-trimethylsilyl)-3-ethylindene (2.16 g, 10 mmol) with $TiCl_4$ (11 ml, 11 mmol) in a manner analogous to the procedure for 1. M.p. 83–84 °C. ^1H NMR (CDCl₃, 200.13 MHz): δ 7.80 (d, $J = 1.06$ Hz, 1H), 7.76 (d, $J = 1.04$ Hz, 1H), 7.50 (m, 2H), 7.11 (d, $J = 3.20$ Hz, 1H), 6.98 (d, $J = 3.44$ Hz, 1H), 3.20 (m, 2H), 1.40 (t, $J_{1,2} = J_{3,2}$ = 7.51 Hz, 3H). $^{13}C\{^1H\}$ NMR (CDCl₃, 50.32 MHz): δ 140.1, 131.4, 130.2, 129.43, 129.40, 127.7, 125.1, 121.6, 116.4, 23.37, 13.57. IR (Nujol mull) cm^{-1}: 599 w, 679 w, 736 m, 752 s, 782 w,

830 s, 901 m, 953 m, 995 m, 1015 w, 1055 m, 1070 m, 1155 w, 1204 m, 1259 m, 1306 m, 1531 w, 1609 w, 1655 w, 1801 w, 3084 w. UV (benzene) λ_{max} (ε, 1cm^{-1} mol^{-1}): 407 nm (3000), 536 nm (1500). MS (m/e, % intensity): 296 (100, M$^+$), 261 (46, M $-$ Cl$^+$), 225 (55, M $-$ 2Cl$^+$), 142 (66, M $-$ 3Cl $-$ Ti$^+$), 127 (67, M $-$ 3Cl $-$ Ti $-$ CH$_3^+$), 115 (55, indene$^+$). Anal. Found: C, 45.18; H, 3.67. C$_{11}$H$_{11}$Cl$_3$Ti. Calc.: C, 44.42; H, 3.73%.

2.6. (1-Trimethylsilyl)-3-isopropylindene

(1-Trimethylsilyl)-3-isopropylindene was prepared in a yield of 67% (2.30 g) by reacting 3-isopropylindene (2.37 g, 11 mmol) with chlorotrimethylsilane (2.14 ml, 16.5 mmol) in a manner analogous to the procedure for (1-trimethylsilyl)-3-ethylindene. ^{1}H NMR (CDCl$_3$, 200.13 MHz): δ 7.47–7.16 (m, 4H), 6.29 (s, 1H), 3.38 (s, 1H), 3.03 (m, 1H), 1.32 (d, $J = 5.44$ Hz, 3H), 1.28 (d, $J = 5.43$ Hz, 3H), -0.05 (m, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$, 50.32 MHz): δ 148.5, 146.4, 143.9, 127.1, 124.4, 123.4, 122.9, 119.3, 44.27, 26.98, 22.79, 21.94, -2.509.

2.7. (η^5-1-Isopropylindenyl)trichlorotitanium (4)

A dark red solid **4** was prepared in a yield of 86% (2.40 g) by reacting (1-trimethylsilyl)-3-isopropylindene (2.07 g, 9 mmol) with TiCl$_4$, (9.9 ml, 9.9 mmol) in a manner analogous to the procedure for 1. M.p. 98–100°C. ^{1}H NMR(CDCl$_3$, 300.13 MHz): δ 7.83–7.48 (m, 4H), 7.05 (d, $J = 3.33$ Hz, 1H), 7.01 (d, $J = 3.40$ Hz, 1H), 3.74 (m, 1H), 1.52 (d, $J = 6.81$ Hz, 3H), 1.30 (d, $J = 7.00$ Hz, 3H). ^{13}C{^{1}H} NMR (CDCl$_3$, 50.32 MHz): δ 145.3, 131.4, 129.6, 129.3, 129.2, 128.0, 125.0, 119.2, 116.9, 29.71, 24.42, 20.70. IR (Nujol mull) cm^{-1}: 643 w, 756 s, 831 s, 903 w, 1000 w, 1048 m, 1069 m, 1126 w, 1204 m, 1290 m, 1531 m, 1560 w, 1606 w, 1656w, 1686 w, 1803 m, 3088 w, 3107 w. UV (benzene) λ_{max} (ε, 1cm^{-1} mol^{-1}): 411 nm (2570), 536 nm (1200). MS (m/e, % intensity): 310 (29, M$^+$), 275 (11, M $-$ Cl$^+$), 224 (39, M $-$ Cl $-$ ^{i}Pr$^+$), 158 (100, M $-$ 3Cl $-$ Ti$^+$), 141 (90, M $-$ 3Cl $-$ Ti $-$ CH$_3^+$), 115 (96, indene$^+$). Anal. Found: C, 46.44; H, 4.07. C$_{12}$H$_{13}$Cl$_3$Ti. Calc.: C, 46.27; H, 4.21%.

2.8. (η^5-(1-Trimethylsilyl)indenyl)trichlorotitanium (5)

A dark red solid **5** was prepared in a yield of 74% (2.53 g) by reacting 1,1- or 1,3-bis(trimethylsilyl)indene (2.60 g, 10 mmol) with TiCl$_4$ (11 ml, 11 mmol) in a manner analogous to the procedure for 1. M.p. 85–86°C. ^{1}H NMR (CDCl$_3$, 300.13 MHz): δ 7.90 (d, $J = 8.84$ Hz, 1H), 7.82 (d, $J = 8.42$ Hz, 1H), 7.50 (m, 2H), 7.38 (d, $J = 2.62$ Hz, 1H), 7.24 (d, $J = 3.38$ Hz, 1H), 0.049 (s, 9H). ^{13}C{^{1}H} NMR (CDCl$_3$, 75.1 MHz): δ 137.2, 135.2,

133.7, 129.58, 129.55, 129.53, 128.6, 126.8, 120.1, -0.394. ^{29}Si NMR (CDCl$_3$, 59.6 MHz): -4.09. IR (Nujol mull) cm^{-1}: 606 w, 642 m, 698 w, 760 s, 844 s, 961 w, 998 w, 1061 m, 1125 m, 1149 s, 1165 m, 1202 m, 1255 s, 1296 w, 1345 w, 1528 m, 1605 w, 1848 w, 1968 w, 3081 w, 3114 w. UV (benzene λ_{max} (ε, 1cm^{-1} mol^{-1}): 403 nm (2200), 530 nm (1350). MS (m/e, % intensity): 340 (17, M$^+$), 325 (43, M $-$ CH$_3^+$), 188 (55, M $-$ 3Cl $-$ Ti$^+$), 172 (79, M $-$ 3Cl $-$ Ti $-$ CH$_3^+$), 157 (37, M $-$ 3Cl $-$ Ti $-$ 2CH$_3^+$), 142 (12, M $-$ 3Cl $-$ Ti $-$ 3CH$_3^+$), 115 (100, indene$^+$), 73 (20, Si(CH$_3$)$^+$). Anal. Found: C, 41.60; H, 4.38. C$_{12}$H$_{15}$Cl$_3$SiTi. Calc.: C, 42.19; H, 4.42%.
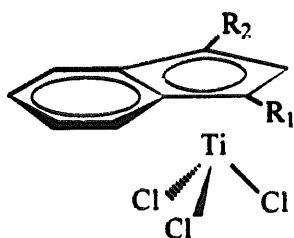
2.9. Polymerization studies

Styrene polymerizations were carried out in a 250 ml Schlenk flask with magnetic stirring. Toluene, the polymerization solvent, was distilled from sodium–potassium alloy under dinitrogen atmosphere just before use. Styrene monomer was distilled from calcium hydride and short-columned in neutral alumina prior to immediate use. The appropriate amount of solid MAO was measured and dissolved in 50 ml of toluene. Then, styrene (5.00 ml, 4.54 g, 43.6 mmol) and the appropriate catalyst were injected into the flask. The polymerizations were performed at 25°C, 50°C, 75°C for 50 min periods. Termination of the polymerizations was effected by the addition of 150 ml of 10% HCl in methanol. The precipitated polymer was washed three times with 50 ml of methanol and dried in vacuo to a constant weight. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the sPS portion of the polymer obtained. For each given polymerization run, two or three serial experiments were carried out to conform the reproducibility of the formation of the polymer and the average values of these serial experimental results are given.

3. Results and discussion

A number of titanium complexes containing monopentahapto-ligand has been studied extensively over the past 30 years [9]. Specifically, the chemistry of CpTiCl$_3$ complex and its derivatives is of interest because they have been evaluated as catalysts for the syndiotactic polymerization of styrene [2]. The previously known mono indenyl titanium halides are rare and include (η^5-C$_9$H$_7$)TiCl$_3$ [3], (η^5-C$_9$Me$_7$)TiCl$_3$ [10] and (phenyl-substituted-Ind)TiCl$_3$ [11]. To take advantage of soluble by-product, 1-trimethylsilyl-substituted indenes were used as indenyl transfer agents [12]; the use of silicon-substituted cyclopentadienyl reagents for the transfer of a single cyclopentadienyl ligand to transition metal is well-known [13]. So the addition of trimethylsi-

lylindenyl derivatives to a room temperature solution of $TiCl_4$ in dichloromethane produces compounds 1–6 in high yields (70–85%) as dark red solids. They were purified by recrystallization from hexane. Like other titanium complexes containing monopentahapto-ligand, all six compounds are air-sensitive and decompose in minutes, both in the solid-state and in solution. They are all readily soluble in toluene, petroleum ether and dichloromethane.

Styrene polymerizations involving compounds 1–6 and MAO as a cocatalyst were performed for various conditions of [Ti], [Al]/[Ti] and polymerization temperature T_p and the polymerization results are summarized in Tables 1 and 2. The percentage of syndiotacticity of the resulting polymers was obtained as their insoluble portion in 2-butanone. ^{13}C NMR spectra at 110°C in 1,1,2,2-tetrachloroethane-d_2 were measured to further confirm the syndiotacticity, and a representative spectrum is given in Fig. 1. The signals for methylene, methine and ipso-phenyl carbons appeared at 43.68 ppm, 40.51 ppm and 145.36 ppm respectively. The appearance of the ipso-phenyl carbon signal at this particular position is a clear indication of the syndiotacticity, as observed previously [14]. The GPC data of a few selected sPS samples indicate that number- and weight-average molecular weights are in the range of 5×10^4 to 2×10^5.

In the case of the reference compound 6, the highest catalytic activity A was observed for the polymerization condition of [Ti] = 40 μM, [Al]/[Ti] = 2000 and $T_{p.}$ = 50°C as listed in Table 2. The A and the polymerization condition of 6–MAO measured in this study are slightly different from the previously reported results, presumably mainly owing to the use of a different source of MAO [3]. For the systems of 1–MAO to 5–MAO, the most efficient polymerization conditions were found to be the same as that of the 6–MAO system, except for 5–MAO where the highest activity was observed at the higher temperature of 75°C. In all cases, the effect of the MAO concentration on the A for a given T_p is that a monotonous increase of [MAO] causes an initial increase, reaching a maximum at around [Al]/[Ti] values of 2000 or 3000, then a decrease in the A. The decline of the A at higher amounts of MAO may be ascribed to excessive alkylation or decomposition of the titanium compounds.

1 $R_1 = CH_3$; $R_2 = CH_3$ 4 $R_1 = CH(CH_3)_2$; $R_2 = H$

2 $R_1 = CH_3$; $R_2 = H$ 5 $R_1 = SiMe_3$; $R_2 = H$

3 $R_1 = CH_2CH_3$; $R_2 = H$ 6 $R_1 = H$; $R_2 = H$

The ^{1}H NMR spectrum of 6 is interpreted as a typical η^5-indenyl pattern in which there is an AA'BB' pattern for the six-membered ring protons and an AB_2 pattern for the five-membered ring protons (^{1}H NMR data for compound 6 ($CDCl_3$, 200.13 MHz) δ 7.80 (m, 2H), 7.50 (m, 2H), 7.20 (d, J = 3.30 Hz, 2H), 7.11 (t, $J_{1,2} = J_{3,2} = 3.29$ Hz); ^{13}C NMR ($CDCl_3$, 200.13 MHz) δ 130.9, 129.9, 127.1, 123.4, 117.1). Other compounds 1–5 shows similar ^{1}H NMR spectra patterns. (See the Section 2).

Table 1
Styrene polymerization catalyzed by 1–MAO to 3–MAO

T_p (°C)	[Al]/[Ti] [a]	1–MAO			2–MAO			3–MAO		
		PS [b] (mg)	$10^{-6}A$ [c]	SY [d]	PS [b] (mg)	$10z^{-6}A$ [c]	SY (%) [d]	PS [b] (mg)	$10^{-6}A$ [c]	SY [d]
25	1000	13	0.179		16	0.220		14	0.193	
25	2000	72	0.993		24	0.331		18	0.248	
25	3000	35	0.484		22	0.303		15	0.207	
50	1000	164	2.26	95.7	84	1.16	95.3	56	0.772	95.8
50	2000	389	5.37	96.1	217	2.99	95.4	174	2.40	96.0
50	3000	120	1.66	95.8	117	1.61	94.0	150	2.07	95.3
75	1000	132	1.82	96.4	86	1.19	90.5	77	1.64	93.5
75	2000	380	5.24	94.7	190	2.62	94.1	147	2.03	94.0
75	3000	124	1.71	94.3	114	1.57	93.6	90	1.24	89.8

[a] [Ti] = 40 μM. [b] PS = polystyrene. [c] Activity = (grams of PS)/((mol of Ti) × (mol of styrene) × (hour)). [d] SY (% of syndiotacticity) = (grams of 2-butanone-insoluble PS)/(grams of PS) × 100.
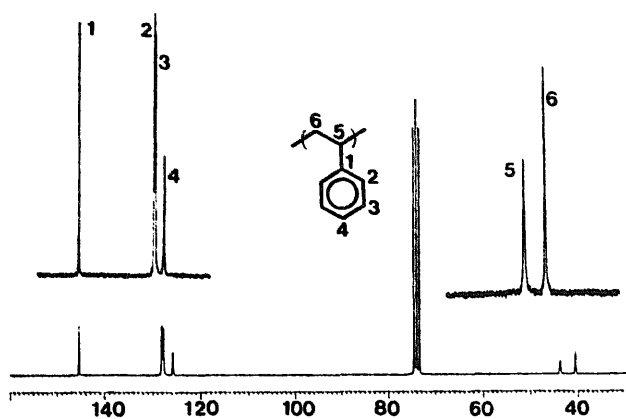
Fig. 1. A representative ^{13}C{^{1}H}NMR spectrum of polystyrene in 1,1,2,2-tetrachloroethane-d_2.

The influence of the substituents of the indenyl ligands on the catalytic activity can be deduced by comparing the polymerization data given in Tables 1 and 2: The catalytic activity increases approximately in the order of 5–MAO < 4–MAO ~ 3–MAO ~ 6–MAO < 2–MAO < 1–MAO. According to Zambelli and coworkers [15], the syndiotactic-specific polymerization

of styrene might be an 'electrophilic' polyinsertion reaction at the metal center, suggesting that titanium compounds with metal centers rich in electron density would be more effective catalysts. In order to probe how the substituents of the indenyl ligand affect the electronic properties of metal centers, the ^{47,49}Ti NMR and electronic spectra of the compounds 1 to 6 were examined.

The UV–vis spectra of all compounds exhibit two absorption maxima, a stronger absorbance between 400 and 410 nm, and a weaker one between 520 and 560 nm. The spectral pattern and trend of those substituted indenyltrichlorotitanium compounds are similar to those observed for ring-substituted titanocene dichlorides [16,17]. In the case of titanocene dichlorides, the red shift [17] of the weaker band at the lower energy region, which has been assigned to a symmetry-forbidden $A_1 \rightarrow A_2$ transition [16], occurs as electron-donating substituents are introduced to the cyclopentadienyl rings. A trend of the similar red-shift seen in the substituted indenyltrichlorotitanium compounds 1 to 6, summarized in Table 3, may suggest that the electron-donating ability of the substituted indenyl ligands increases in the order of 6 < 5 < 4 ~ 3 ~ 2 < 1.

Table 2
Styrene polymerization catalyzed by 4–MAO to 6–MAO

T_p (°C)	[Al]/[Ti] [a]	4–MAO			5–MAO			6/MAO		
		PS [b] (mg)	$10^{-6}A$ [c]	SY (%) [d]	PS [b] (mg)	$10^{-6}A$ [c]	SY (%) [d]	PS [b] (mg)	$10^{-6}A$ [c]	SY (%) [d]
25	1000	10	0.138		5	0.069		16	0.221	
25	2000	29	0.400		16	0.221		25	0.345	
25	3000	58	0.800	94.8	14	0.193		38	0.524	
25	4000	34	0.469					42	0.579	
50	1000	32	0.441		24	0.331		54	0.745	90.1
50	2000	117	1.61	94.0	114	1.57	94.7	170	2.34	94.1
50	3000	230	3.17	91.3	57	0.786	92.1	75	1.03	95.6
50	4000	60	0.828	91.7				62	0.855	91.1
75	1000	48	0.662	91.5	76	1.05	90.8	76	1.05	90.8
75	2000	116	1.60	95.7	121	1.67	91.7	93	1.28	94.7
75	3000	152	2.10	95.4	72	0.993	91.5	121	1.67	95.7
75	4000	123	1.70	93.5				148	2.04	96.4

[a] [Ti] = 40 µM. [b] PS = polystyrene. [c] Activity = (grams of PS)/((mol of Ti) × (mol of styrene) × (hour)). [d] SY (% of syndiotacticity) = (grams of 2-butanone-insoluble PS)/(grams of PS) × 100.

Table 3
Absorption maxima of lowest energy transitions in the UV–vis spectra and Ti NMR chemical shifts and line widths of compounds 1–6

Compound [a]	λ (nm)	ε (l cm^{-1} mol^{-1})	δ^{49}Ti [b] (ppm)	$\Delta\nu_{1/2}(^{49}$Ti) [c] (Hz)	δ^{47}Ti [b] (ppm)	$\Delta\nu_{1/2}(^{47}$Ti) [c] (Hz)
TiCl$_4$			0	3 ± 0.5	–266.4	10 ± 1
1	561	1050	–114.1	230 ± 5	–391.7	> 1000
2	538	1200	–197.3	280 ± 7	–461.5	> 1000
3	536	1500	–191.8	374 ± 10	–438.3	> 1000
4	536	1200	–197.4	382 ± 10	–455.6	> 1000
5	530	1350	–236.8	360 ± 10	–481.1	> 1000
6	521	1480	–268.6	184 ± 5	–530.3	548 ± 15

[a] 1 × 10^{-3} M solution in benzene. [b] ^{49}Ti and ^{47}Ti chemical shifts are given relative to external ^{49}TiCl$_4$. [c] Mean value and standard deviation of three independent measurements.
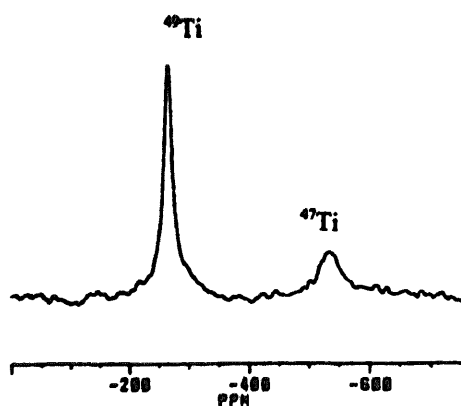
Fig. 2. Ti NMR spectrum of compound 6.

The ^{47,49}Ti NMR spectral data also provide a similar ligand trend for the electron-donating ability. Summarized in Table 3 are ^{47}Ti and ^{49}Ti NMR chemical shifts and line widths measured for the saturated solutions of compounds 1 to 6 in $CDCl_3$ at 323 K. The Ti NMR measurement temperature of 323 K was chosen since most of catalytic systems of compounds 1–MAO to 6–MAO showed the highest polymerization activity at this T_p. As illustrated in Fig. 2, the ^{49}Ti resonance appears approximately 270 ppm downfield of the ^{47}Ti resonance. Owing to its higher quadrupole moment, the ^{47}Ti resonance is always broader than the ^{49}Ti resonance [18] and both Ti resonances of the substituted indenyltrichlorotitanium compounds are much broader than those of substituted cyclopentadienyl analogues. In general, chemical shift values of Ti NMR display the electron distribution around the titanium center in a series of structurally analogous complexes and the line widths were found to reflect the sterically induced electronic asymmetry around the titanium atom [19]. In particular, the Ti NMR chemical shifts are inversely related to the electronegativity of the halide ligands at titanium, known as an inverse halogen dependence [20], suggesting that the introduction of the electron-donating substituents into the indenyl ligands will cause a downfield-shift of the Ti resonances. Then, the data given in Table 3 clearly indicate that the electron-donating ability of the substituted indenyl ligands also increases in the order of $6 < 5 < 4 \sim 3 \sim 2 < 1$ and the sterically induced electronic asymmetry is larger for 3, 4 and 5 compared with the others.

If the electronic properties of metal centers, and thereby the electron-donating ability of the substituted indenyl ligands, are the only governing factors determining the catalytic efficiency of compounds 1 to 6 in the syndiotactic-specific polymerization of styrene, the Ti NMR and electronic spectral data would give a catalytic order of $6-MAO < 5-MAO < 4-MAO \sim 3-MAO \sim 2-MAO < 1/MAO$ which is somewhat different from the polymerization results of $5-MAO < 4-$

$MAO \sim 3-MAO \sim 6-MAO < 2-MAO < 1-MAO$, suggesting that other factors, such as, among others, the steric effect of substituted indenyls, are also an important governing key to the order of the catalytic activities. In the case of mono-substituted indenyl compounds, the steric bulkiness of indenyl ligands increases in the order $2 < 3 < 4 < 5$ from 1. Coupled use of this steric trend and the aforementioned electronic trend in interpreting the measured order of the catalytic activities would provide some qualitative gage in determining the relative importance of both factors. The trimethylsilyl group in compound 5 would increase both electron density and steric hindrance on the indenyl ring, and hence would lead to the low activity and higher polymerization temperature. In fact, the 5–MAO system constitutes the lowest in the order of the catalytic activities and requires a higher polymerization temperature of 75 °C compared with the others.

4. Conclusions

Substituents in the substituted indenyltrichlorotitanium compounds impose electronic and steric effects to different extents on the metal centers of catalysts involved in the syndiotactic-polymerization of styrene. This affects the catalytic activities and polymerization conditions. The UV–vis and ^{47,49}Ti NMR spectra provided a consistent measure of the electron densities at the metal centers of six indenyltrichlorotitanium compounds. The overall catalytic activity is enhanced by introduction of less-bulky and better electron-donating substituents into the indenyl ring.

Acknowledgements

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