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Journal of Organometallic Chemistry 627 (2001) 233–238

Journal of Organometallic Chemistry

www.elsevier.nl/locate/jorganchem

Synthesis of titanium trichloride complexes of 1,2,3-trisubstituted cyclopentadienyls and their use in styrene polymerization

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Received 15 June 2000; received in revised form 26 February 2001; accepted 27 February 2001

Abstract

The synthesis, characterization and styrene polymerization properties of titanium trichloride compounds (**5**, 1,3-dimethyl-2-*n*-butylcyclopentadienyl; **6**, 1,3-dimethyl-2-*t*-butylcyclopentadienyl; **13**, 1,3-diphenyl-2-*n*-butylcyclopentadienyl; **14**, 1,3-dimethyl-2-phenylcyclopentadienyl; **15**, 1,2,3-triphenylcyclopentadienyl) containing 1,2,3-trisubstituted cyclopentadienyl ligands are reported. Reactions of lithiated cyclopentadienide with Me_3SiCl followed by addition of $TiCl_4$ gave new titanium trichloride compounds **5** and **6**, respectively, in reasonable yields, and reactions of cyclopentadiene with $Ti(NMe_2)_4$ followed by Me_3SiCl or Me_2SiCl_2 gave new titanium trichloride compounds **13**–**15**, respectively, in reasonable yields. Compound **14** has been characterized by single crystal X-ray diffraction studies: monoclinic space group $P2_1/c$; $a = 15.893(2)$, $b = 7.199(1)$, $c = 12.812(2)$ Å, $\beta = 108.394(7)°$, $Z = 4$ and $V = 1390.9(3)$ Å^3. The catalytic behavior of the new titanium compounds in styrene polymerization has been studied in the presence of excess methylaluminoxane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyclopentadienyl; Titanium; Styrene; Polymerization; Syndiotactic

1. Introduction

Since Ishihara et al. reported the first preparation of syndiotactic polystyrene (s-PS) using the $CpTiCl_3/MAO$ catalyst system [1,2], a wide variety of new catalytic systems based on titanium or zirconium compounds have been synthesized and studied as s-PS catalyst [3–13]. Among those complexes, Cp^*TiX_3, (indenyl)$TiCl_3$, and (substituted indenyl)$TiCl_3$ derivatives are the most active catalysts. Studies on the mechanism involved in the polymerization of styrene have also been reported [14–18].

The chemical and physical properties of cyclopentadienyl titanium complexes can be varied over a wide range by modification of the substituents on the cyclopentadienyl ring [19]. Thus, many research groups are involved in the design of ligands to tailor the catalytic activity and product properties. However, a limited range of cyclopentadienyl titanium complexes containing such ligands have been prepared and studied due to the absence of a generalized synthetic method for substituted cyclopentadiene. Recently, Takahashi et al. [20] reported the synthesis of 1,2,3-trisubstituted cyclopentadienes through the reaction of zirconacyclopentene with acid chloride in the presence of a catalytic amount of copper chloride. Several years ago, we reported [21] the general method for preparation of 1,2,3-trisubstituted cyclopentadienyls and their use in the preparation of manganese tricarbonyl and zirconium dichloride derivatives. The method can be easily extended to synthesize 1,2,3-trisubstituted cyclopentadienyl titanium trichlorides. Herein we report the synthesis and characterization of 1,2,3-trisubstituted cyclopentadienyl titanium trichloride and their behavior in styrene polymerization.

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PII: S0022-328X(01)00749-5

2. Experimental

2.1. General

Reactions were carried out under argon or nitrogen atmosphere using standard Schlenk techniques or in a glove box. Methylaluminoxane (MAO) was purchased from Akzo (6.4 wt.% of Al, MMAO type 4). Chlorotrimethylsilane, dichlorodimethylsilane, and styrene were purified by distillation over CaH_2. Hexane and toluene were purified over Na/K alloy under argon. ^{1}H-NMR and ^{13}C-NMR spectra were recorded on a Bruker DPX-300 spectrometer. Elemental analyses were done at the National Centre for Inter-University Research Facilities, Seoul National University. T_m was measured on a Thermal Analysis 3100. Gel permeation chromatograms (GPC) were obtained at 140°C in trichlorobenzene using Waters model 150-C + GPC and the data were analyzed using a polystyrene analyzing curve. All trisubstituted cyclopentadienes **1**, **2**, and **7**–**9** were synthesized by the previously published procedures [21].

2.2. Synthesis of **5**

To a solution of **1** (0.78 g, 5.19 mmol) in 10 ml of THF was added *n*-BuLi (5.19 mmol) at −78°C. The solution was slowly warmed to room temperature (r.t.). After the solution was stirred for 4 h at r.t., $ClSiMe_3$ (0.70 ml) was added. After the solution was stirred overnight, the solvent was removed at reduced pressure. To the residue was added 30 ml of hexane. Filtration and evaporation gave an oily compound **3**.^{1}H-NMR ($CDCl_3$): δ 5.86 (br s, 1 H), 2.91 (br s, 1 H), 2.28–2.25 (m, 2 H), 1.96 (s, 6 H), 1.4–1.3 (m, 4 H), 0.92 (t, 6.7 Hz, 3 H), −0.05 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 141.49, 139.77, 137.49, 124.79, 51.35, 32.37, 25.50, 22.86, 14.87, 14.04, −2.00 ppm. Anal. Found: C, 75.10; H, 11.31. Calc. for $C_{14}H_{26}Si$: C, 75.59; H, 11.78%. To **3** (0.926 g, 4.17 mmol) was added 20 ml of CH_2Cl_2. The solution was cooled to −78°C. $TiCl_4$ was added to the cold solution and the resulting solution was warmed to r.t. After the solution was stirred for 4 h at r.t., all volatiles were removed at reduced pressure to give yellowish red solids **5** (1.06 g, 77%). ^{1}H-NMR ($CDCl_3$): δ 6.71 (s, 2 H), 2.77 (t, 7.6 Hz, 2 H), 2.40 (s, 6 H), 1.5–1.3 (m, 4 H), 0.93 (t, 6.9 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 141.19, 139.07, 123.74, 31.64, 28.17, 22.78, 16.20, 15.26, 13.84 ppm. HRMS *m*/*e*, M^+, obsd. 301.9884, calc. 301.9875.

2.3. Synthesis of **6**

The same procedure as for the synthesis of **5** was applied. The yield of **4** from **2** was 75%. ^{1}H-NMR ($CDCl_3$) of **4**: δ 5.86 (br s, 1 H), 2.89 (br s, 1 H), 2.13 (br s, 6 H), 1.30 (s, 9 H), −0.05 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$) of **4**: δ 144.16, 142.65, 136.80, 128.10, 54.13, 34.84, 31.55, 18.96, 18.56, −1.88 ppm. Red crystalline solids **6** were obtained from **4** in 80% yield. ^{1}H-NMR ($CDCl_3$) of **6**: δ 6.55 (s, 2 H), 2.66 (s, 6 H), 1.46 (s, 9 H) ppm. ^{13}C-NMR ($CDCl_3$) of **6**: δ 149.05, 139.28, 126.63, 37.04, 30.90, 20.90 ppm. HRMS *m*/*e*, M^+, obsd. 301.9881, calc. 301.9875.

2.4. Synthesis of **13**

To a solution of **7** (0.372 g, 1.36 mmol) in 10 ml of toluene was added $Ti(NMe_2)_4$ (0.32 ml, 1.36 mmol). As the reaction went on, the evolution of $NHMe_2$ was observed. The solution was stirred at 70°C for 4 h at which time evolution of the gas ceased. All volatiles were removed at reduced pressure to give a red oily compound **10**. As $ClSiMe_3$ (5 ml) was added to **10** at r.t., the solution changed to deep red. The resulting solution was heated to 50°C for 18 h. After the solution was cooled to r.t., the solution was evaporated to dryness. Hexane (20 ml) was added to the residue and the solution was filtered. The clear solution was kept in a refrigerator (at −30°C). Reddish crystalline solids were deposited. The isolated yield of **13** was 40% (0.23 g). ^{1}H-NMR ($CDCl_3$): δ 7.7–7.3 (m, 10 H), 7.29 (s, 2 H), 3.31 (t, 7.5 Hz, 2 H), 1.1–0.9 (m, 4 H), 0.57 (t, 7.1 Hz, 3 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 141.68, 138.09, 133.79, 129.31, 129.04, 128.75, 122.95, 30.72, 27.77, 22.17, 13.34 ppm. Anal. Found: C, 59.16; H, 4.20. Calc. for $C_{21}H_{21}Cl_3Ti$: C, 58.98; H, 4.95%. HRMS *m*/*e*, M^+ obsd. 426.0204, calc. 426.0188.

2.5. Synthesis of **14**

To a solution of **8** (0.276 g, 1.62 mmol) in 5 ml of toluene was added $Ti(NMe_2)_4$ (0.38 ml, 1.62 mmol). The solution was heated at 50°C for 18 h. Removal of all the volatiles gave **11**. ^{1}H-NMR ($CDCl_3$): δ 7.4–7.2 (m, 5 H), 5.84 (s, 2 H), 3.01 (s, 18 H), 2.15 (s, 6 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 136.31, 130.60, 127.93, 125.73, 124.55, 121.99, 108.76, 48.78, 14.51 ppm. As Cl_2SiMe_2 (10 ml) was added to **11** at r.t., the solution changed to deep red. The resulting solution was heated to 70°C for 3 h. All the volatiles were evaporated and the residue was extracted with 40 ml of hot hexane. The hexane solution was filtered and cooled to r.t. to precipitate the product. Red crystalline solids **14** were isolated (0.388 g, 74%). Single crystals of **14** suitable for X-ray study were grown in hexane at r.t. ^{1}H-NMR ($CDCl_3$): δ 7.5–7.3 (m, 5 H), 6.57 (s, 2 H), 2.46 (s, 6 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 138.02, 136.88, 132.42, 130.25, 128.37, 128.31, 121.98, 16.46 ppm. Anal. Found: C, 48.27; H, 4.05. Calc. for $C_{13}H_{13}Cl_3Ti$: C, 48.27; H, 3.81%.

2.6. Synthesis of **15**

The same procedure as for the synthesis of **14** was applied. ^{1}H-NMR ($CDCl_3$) of **12**: δ 7.4–7.3 (m, 5 H), 7.1–7.0 (m, 9 H), 6.41 (s, 2 H), 3.03 (s, 18 H) ppm. ^{13}C-NMR ($CDCl_3$) of **12**: δ 137.21, 137.07, 132.51, 129.14, 128.32, 128.14, 128.00, 127.68, 126.98, 126.36, 124.74, 49.73 ppm. The yield of **15** from **12** was 50%. Compound **15** was purified by recrystallization in toluene at −30°C. ^{1}H-NMR ($CDCl_3$): δ 7.4–7.2 (m, 6 H), 7.0–6.8 (m, 9 H), 6.75 (s, 2 H) ppm. ^{13}C-NMR ($CDCl_3$): δ 141.01, 135.86, 133.31, 132.72, 131.85, 129.81, 129.41, 128.58, 128.32, 122.42 ppm. Anal. Found: C, 61.58; H, 3.83. Calc. for $C_{23}H_{17}Cl_3Ti$: C, 61.72; H, 3.83%.

2.7. Polymerization

To a Schlenk flask was added successively toluene (40 ml), styrene (5.0 ml), and MAO (5.0 ml, 10 mmol of Al). The solution was immersed into a preheated oil bath (at 50, 75, and 100°C). After the solution was stirred for 10 min, a catalyst (2.5 μmol in toluene solution) was added with vigorous stirring. After 10 min, 50% HCl in methanol solution (20 ml) was carefully added via a syringe. As the reaction mixture was cooled to r.t., solids were suspended. The solids were filtered, washed with methanol, and dried at 100°C. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the s-PS portion of the polymer obtained.

Table 1
X-ray data collection and structure refinement for **14**

Formula	$C_{13}H_{13}Cl_3Ti$
Formula weight	323.48
Temperature (K)	294(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	15.893(2)
b (Å)	7.199(1)
c (Å)	12.812(2)
β (°)	108.394(7)
V (Å^3)	1390.9(3)
Z	4
d_{calc} (g cm^{-3})	1.545
μ (mm^{-1})	1.165
$F(000)$	656
T_{min}	0.2993
T_{max}	0.3951
2θ range (°)	3.5–50
Scan type	ω
Scan speed	Variable
Reflections measured	2572
Unique reflections	2449
Reflections with $I>2\sigma(I)$	2086
Parameters refined	207
Maximum, in $\Delta\rho$ (e Å^{-3})	0.361
Miniimum, in $\Delta\rho$ (e Å^{-3})	−0.301
GOF on F^2	1.027
R	0.0345
wR_2 [a]	0.0897

[a] $wR_2 = \Sigma[w(F_o^2-F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

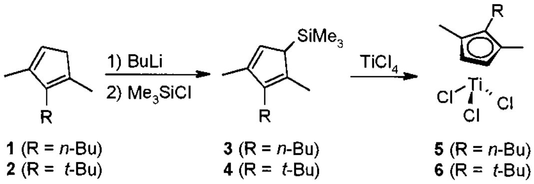
2.8. X-ray crystal structure determination of **14**

All X-ray data were collected using a Siemens P4 diffractometer equipped with a Mo X-ray tube and a graphite crystal monochromator. The orientation matrix and unit cell parameters were determined by least-squares analyses of the setting angles of 33 reflections in the range $10.0° < 2\theta < 25.0°$. Three check reflections were measured every 100 reflections throughout data collection and showed no significant variation in intensity. Intensity data were corrected for Lorentz and polarization effects. Decay corrections were also made. The intensity data were corrected empirically with ψ-scan data. All calculations were carried out with use of the SHELX-97 programs. The unit cell parameters and systematic absences, $h0l$ ($l = 2n + 1$) and $0k0$ ($k = 2n + 1$), indicated unambiguously the $P2_1/c$ space group. The structure was solved by the direct method and refined by full-matrix least-squares calculations, initially with isotropic and finally anisotropic temperature factors for all non-hydrogen atoms. All hydrogen atoms were located in the difference Fourier map and refined isotropically. Crystal data, details of the data collection, and refinement parameters are listed in Table 1.

3. Results and discussion

3.1. Synthesis

Compound **5** was prepared by treatment of pure anhydrous $TiCl_4$ with **3** in methylene dichloride, a well known and routine technique (Eq. (1)) [3,5–11,19d,22].



(1)

Compound **3** was obtained by reaction of **1** with n-BuLi and chlorotrimethylsilane. The overall yield from **1** to **5** was 77%. In the same way, **6** was synthesized with overall yield of 75%. Treatment of cyclopentadienes bearing phenyl group(s) with $TiCl_4$ yielded untraceable black precipitates that might be due to the reduction of $TiCl_4$ to $TiCl_3$. The phenyl group may help the electron transfer from the cyclopentadiene to titanium tetrachloride. Thus, the synthetic method de-

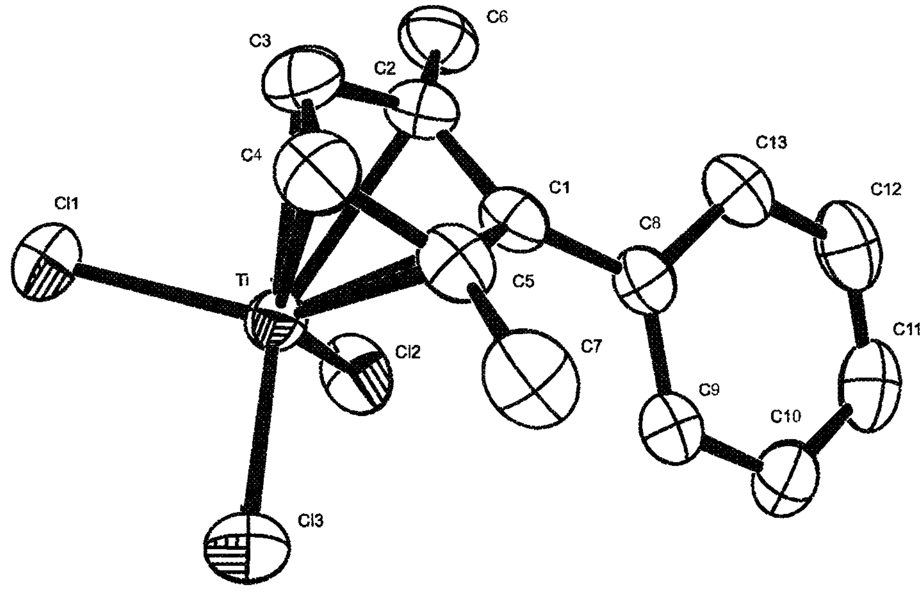
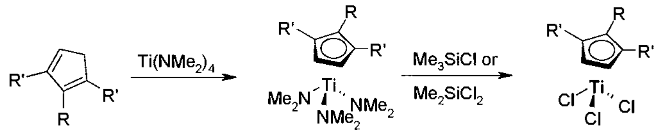


Fig. 1. Molecular structure of compound **14**, with the atom-labeling scheme.

scribed above seems to be confined to the synthesis of titanium chloride complexes of alkyl substituted cyclopentadienyls.

Titanium chloride compounds **13**–**15** having a phenyl group(s) were synthesized by the method shown in Eq. (2).



7 (R = *n*-Bu, R' = Ph)
8 (R = Ph, R' = Me)
9 (R = R' = Ph)

10 (R = *n*-Bu, R' = Ph)
11 (R = Ph, R' = Me)
12 (R = R' = Ph)

13 (R = *n*-Bu, R' = Ph)
14 (R = Ph, R' = Me)
15 (R = R' = Ph)

(2)

Treatment of cyclopentadienes **7**–**9** with Ti(NMe$_2$)$_4$ resulted in the formation of amido complexes **10**–**12** [23]. Complexes **10**–**12** could be transformed to the corresponding trichloride complexes via reaction with appropriate chlorinating reagents. However, there was no general method to chlorinate all the amido complexes. Treatment of **10** with chlorotrimethylsilane at ambient temperature in toluene gave a product having two chloride groups. When chlorination of **10** was carried out in neat chlorotrimethylsilane at 50°C, the desired trichloride complex **13** was obtained. Compounds **14** and **15** were obtained when dichlorodimethylsilane was used as a chlorinating reagent.

3.2. X-ray analysis

Single crystals of **14** suitable for X-ray crystal structure determination were grown in hexane at room temperature. Fig. 1 gives an ORTEP view of the structure of **14** together with the atom labeling. Selected bond distances and angles for the coordination geometry of the titanium atom are given in Table 2.

The coordination polyhedron about the Ti atom is a distorted tetrahedron formed by three Cl atoms and one Cp ring. The Ti–Cp-ring centroid bond distance is 2.029 Å. The phenyl ring (C8–C13) is tilted with respect to the cyclopentadienyl ring with a dihedral angle of 44.49(8)°. The Ti–Cp-ring carbon distances indicate that the Ti–Cp-ring interaction is asymmetric. The distances are in the range 2.310–2.403 Å. For other (η^5-RC$_5$H$_4$)TiCl$_3$, the Ti–Cp-ring carbon distance is longest for the carbon atom bonded to the substituent group [8,24]. In **14**, C1 and C5 form longer distances with the Ti atom than the other Cp-ring carbon atoms. The reason why C5 forms a longer distance with the Ti atom is due to the tilt of the phenyl group toward C5. The Ti–Cl bond distances are in the typical range at Ti–C = 2.230 Å (average).

3.3. Polymerization

Compounds **5**, **6**, and **13**–**15** were tested for the polymerization of styrene with MAO as a cocatalyst. For comparison, Cp*TiCl$_3$ was also used as a polymerization catalyst under identical conditions. The results are shown in Table 3. The trisubstituted cyclopentadienyl titanium compounds showed higher activities than Cp*$TiCl_3$. The highest activity was obtained with **14** at 75°C. At 50°C, molecular weights (M_w) of the polymers obtained with **5**, **6** and Cp*$TiCl_3$ were 54 000–68 000 at 50°C but those for **13**, **14** and **15** bearing phenyl substituents were 79 000, 40 000 and 25 000, respectively. The phenyl substituents on the cyclopentadienyl ligand in **13** increased the activity as seen in indenyl titanium trichloride complexes [8,11]. Titanium compounds having a phenyl group(s) on the cyclopentadienyl ring also showed higher activities than those having only alkyl groups on the cyclopentadienyl ring. Rausch et al. [11] explained the enhanced activities of phenyl-substituted indenyl complexes as the increased resonance stabilization. However, complexes **13**, **14** and **15** showed quite different activities. The decreased activity for **15** was presumably due to the steric problem as in (indenyl)$TiCl_3$ derivatives [11]. Complex **15** was completely inactive at 100°C.

As the reaction temperature increased, the syndiotactic yields, measured by extraction with refluxing 2-butanone, decreased for all compounds. Up to 75°C, the syndiotactic yields remained above 90% except for **15** which showed low syndiotactic yield (76%) at 75°C. At 100°C, the syndiotactic yields for **6**, **14** and Cp*$TiCl_3$ dropped to 73–77%, but those for **5** and **13** were still 88–90%.

Molecular weights decreased as the reaction temperature increased. Narrow molecular weight distributions (M_w/M_n, 1.7–2.2) imply that the polymers were prepared by single-site catalysts. The values and trends of

Table 2
Selected bond distances (Å) and bond angles (°) in **14**

Ti–Cl3	2.2237(8)	Ti–Cl1	2.2258(8)	Ti–Cl2	2.2415(8)
Ti–C3	2.310(3)	Ti–C4	2.316(3)	Ti–C2	2.364(2)
Ti–C1	2.401(2)	Ti–C5	2.403(3)	C1–C2	1.428(4)
C1–C5	1.429(3)	C1–C8	1.480(4)	C2–C3	1.409(4)
C2–C6	1.500(4)	C3–C4	1.393(4)	C4–C5	1.415(4)
C5–C7	1.493(4)	Ti–Cp(1) [a]	2.029		
Cl3–Ti–Cl1	101.40(3)	Cl3–Ti–Cl2	103.45(3)		
Cl1–Ti–Cl2	101.75(3)	C2–C1–C5	107.9(2)		
C2–C1–C8	126.5(2)	C5–C1–C8	125.5(2)		
C3–C2–C1	107.4(2)	C3–C2–C6	124.5(3)		
C1–C2–C6	128.1(3)	C4–C3–C2	108.7(3)		
C3–C4–C5	109.2(2)	C4–C5–C1	106.7(2)		
C4–C5–C7	125.4(3)	C1–C5–C7	127.7(3)		
C9–C8–C1	121.2(2)				

[a] Cp(1) refers to the computed centroid of the ring carbons C1–C5.

Table 3
Polymerization of styrene

Catalyst	T_p (°C)	Yield (g)	Activity [a]	T_m (°C)	M_w	M_w/M_n	SY (%) [b]
5	50	0.33	0.79	272	60,000	1.9	93
5	75	1.17	2.8	264	31,000	2.2	89
5	100	1.22	2.9	253	11,000	1.8	88
6	50	0.59	1.4	272	54,000	2.0	99
6	75	0.87	2.1	265	21,000	2.0	96
6	100	0.94	2.3	249	7,500	1.7	73
13	50	0.89	2.1	271	79,000	1.9	95
13	75	1.22	2.9	269	37,000	2.1	90
13	100	1.22	2.9	255	14,000	1.9	90
14	50	1.25	3.0	269	40,000	2.4	96
14	75	1.63	3.9	262	20,000	2.0	92
14	100	1.50	3.6	242	8,200	1.7	75
15	50	0.75	1.8	267	25,000	2.2	94
15	75	0.72	1.7	255	10,000	1.7	76
15	100	0	0				
Cp*$TiCl_3$	50	0.038	0.091	272	68,000	2.0	
Cp*$TiCl_3$	75	0.28	0.67	272	43,000	2.2	91
Cp*$TiCl_3$	100	0.44	1.1	269	18,000	2.0	77

[a] 10^6g/(mol(Ti) $\times$ h).

[b] SY (% of syndiotacticity) = (g of 2-butanone-insoluble PS)/(g of PS) × 100.

T_m with respect to the polymerization temperature were almost identical with the previously reported titanium trichloride complexes [8].

4. Supplementary material

Crystallographic data for structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 158012 for compound **14**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

Acknowledgements

This work was supported by the Korea Science and Engineering Foundation (KOSEF) (1999-1-122-001-5) and the KOSEF through the Center for Molecular Catalysis. J.W.H. and H.S. thank the Ministry of Education for the Brain Korea 21 Fellowship.

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