APPLIED ORGANOMETALLIC CHEMISTRY
Appl. Organometal. Chem. 2003; **17**: 277–281 **Materials, Nanoscience and Catalysis** **AOC**

Syndiotactic polymerization of styrene catalyzed by alkenyl-substituted cyclopentadienyltitanium trichlorides

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Received 24 October 2001; Revised 23 January 2003; Accepted 25 January 2003

$CH_2{=}CHCH_2CpTiCl_3$ (1), $CH_2{=}CHCH_2CH_2CpTiCl_3$ (2) and $CH_3CH_2CH_3CpTiCl_3$ (3) have been synthesized and characterized. The influence of the alkenyl substituent groups on the catalyst activities in the syndiotactic polymerization of styrene was investigated. The catalyst activities decreased in the order $CH_2{=}CHCH_2CH_2CpTiCl_3 > CH_3CH_2CH_2CH_2CpTiCl_3 > CH_3CH_2CH_2CpTiCl_3 > CH_2{=}CHCH_2CpTiCl_3$ ($Cp{=}C_5H_4$). By using complex 1, the dependence of the activity on the concentration of methylaluminoxane, triisobutylaluminum and diisobutylaluminum hydride was investigated. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: syndiotactic polymerization; styrene; alkenyl-functional group; half-sandwich titanocene

INTRODUCTION

Since Ishihara and coworkers[1–3] succeeded in the synthesis of syndiotactic polystyrene (s-PS) in 1985 based on titanium compounds and methylaluminoxane (MAO), half-sandwich titanocene (e.g. $CpTiCl_3$, $IndTiCl_3$ (Ind = indenyl) and their analogs) have been demonstrated to be the most effective syndiospecific catalyst precursors of styrene[4–6]. Not only do variations in the cyclopentadienyl- (Cp-) or Ind-ligand periphery often result in dramatic changes in catalyst activity and the physical and chemical properties of the polymer, but so also do variations in the chlorine atom of $CpTiCl_3$ or $IndTiCl_3$; this can be attributed to electronic and steric effects caused by the substituent groups. So, a large number of half-sandwich titanocenes have been synthesized.[7–25]

Generally, most substitutent groups in the Cp- or Ind-ligand are alkyl, phenyl or trimethylsilyl, which could stabilize the active center of the catalyst and increase the molecular weight of s-PS.[26–28] Introduction of oxygen- or nitrogen-containing functional groups in the Cp ligand led to a dramatic reduction of the catalyst activities in the syndiotactic polymerization of styrene, because the strong coordination of the donor atom to the metal blocked the coordination and insertion of styrene.[29–31] Recently, the use of ligands substituted by weaker donor systems, such as alkenyl groups, has focused attention on styrene polymerization,[32,33] although alkenyl-functional group containing half-sandwich titanocenes have been synthesized ($CH_2{=}CHC_pMe_4TiCl_3$,[34] $CH_2{=}CHCH_2CH_2CpMe_4TiCl_3$[35,36]). Here, we report the synthesis of two alkenyl-substituted cyclopentadienyl titanium trichlorides, and compare their catalytic behavior with the corresponding *n*-alkylcyclopentadienyl titanium trichlorides in the syndiotactic polymerization of styrene, in order to investigate the effect of the alkenyl group.

RESULTS AND DISCUSSION

Synthesis of catalyst precursors

As shown in Scheme 1, the reaction of the corresponding substituted cyclopentadienyltrimethylsilane with $TiCl_4$ gave complexes **1** to **3**, which can be recrystallized from hot *n*-hexane as yellow crystals in 42–64% yields. It was found that the product yield in CH_2Cl_2 solution was much higher than that in toluene solution. Complexes **1** to **3** were characterized by elemental analysis, ^{1}H NMR, IR and mass spectra. The ^{1}H NMR results indicate that the resonance for the hydrogen of the vinylgray of complexes **1** and **2** does not shift to higher field (low frequency). In the IR spectra, complexes **1**

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Contract/grant sponsor: Special Funds for Major State Basic Research Projects; Contract/grant number: G1999064801.

$$\mathrm{RCpNa} \xrightarrow[\mathrm{THF}]{\mathrm{Me_3SiCl}} \mathrm{RCpSiMe_3} \xrightarrow[\mathrm{CH_2Cl_2}]{\mathrm{TiCl_4}} \mathrm{RCpTiCl_3}$$

R=CH_2=$CHCH_2$ (**1**)
R=CH_2=$CHCH_2CH_2$ (**2**)
R=$CH_3CH_2CH_2$ (**3**)
R=$CH_3CH_2CH_2CH_2$ (**4**)

Scheme 1.

and **2** show a band at 1640 cm^{-1} due to an uncoordinated $\nu_{C=C}$. These phenomena indicate that the C=C bond of the alkenyl group in complexes **1** and **2** is not coordinated to the metal center.[37]

Polymerization results

Table 1 summarizes the results for the syndiotactic polymerization of styrene with the $RCpTiCl_3$/MAO system at 50 °C. The catalytic activities of complexes **1** to **4** increased with increasing the Al/Ti ratio from 1000 to 4000, which is in agreement with those reported by Ishihara *et al.*[3] At [Ti] = 0.21 M, the polymer obtained showed the highest syndiotacticity. In addition, introduction of an alkenyl or *n*-alkyl group into the Cp-ligand increased the melting points of the polymers. On average, the melting points of the polymers were 8 °C higher than that of the polymer obtained with $CpTiCl_3$.

As shown in Table 1, the chain length and the C=C double bond of substituent group had some influence on the catalytic activities and the syndiotacticities of polymers. Their polymerization activities increased in the order CH_2=$CHCH_2CpTiCl_3$ (**1**) <$CH_3CH_2CH_2CpTiCl_3$ (**3**) <$CH_3CH_2CH_2CH_2CpTiCl_3$ (**4**) <$CpTiCl_3$ < CH_2=$CHCH_2CH_2CpTiCl_3$ (**2**). Complexes **2** and **4**, containing the substituent group with four carbon atoms, showed higher activities and syndiotacticities than the corresponding complexes **1** and **3** containing the substituent group with three carbon atoms. Generally, the stronger electron-donating and less bulky substituent groups are beneficial to the polymerization by increasing the rate of propagation. Complex **1** containing the allyl group exhibited the lowest activity and syndiotacticity. Owing to similar steric effects between the allyl group and the *n*-propyl group, this indicates that the electron-donor ability of the allyl group may be less than that of the *n*-propyl group and, moreover, the C=C bond of the allyl group might coordinate strongly to the active center, as suggested in the literature,[38–40], which interferes with the coordination and the insertion of styrene. Complex **2** containing the 3-butenyl group showed the highest activity and syndiotacticity. It is thought that the C=C bond of the butenyl group might not coordinate to the active center or coordinate much more weakly to the active center, which cannot affect the coordination and the insertion of monomer. The activity of complex **2** was higher than that of complex **4**, although the electric and steric effects between 3-butenyl and *n*-butyl groups are similar. This indicates that the 3-butenyl group may be beneficial in stabilizing the active center and, meanwhile, does not hinder the coordination of the styrene monomer, which leads to an increase in the catalytic activity and syndiotacticity, especially at [Ti] = 0.105 mM. In addition, only complex **2** exhibited higher activity than $CpTiCl_3$. Usually, introduction of a substituent group into the Cp-ligand decreased the catalyst activity[33,41,42].

Table 1. Syndiotactic polymerization of styrene catalyzed by $RCpTiCl_3$/MAO systems[a]

Catalyst	R	[Ti] (mM)	Al/Ti (mol/mol)	Yield (g)	Activity[b] ($\times 10^7$)	s-PS[c] (%)	T_m[d] (°C)
1	CH_2=$CHCH_2$	0.42	1000	0.3581	0.82	92.1	
		0.21	2000	0.2341	1.07	92.2	266.0
		0.105	4000	0.1817	1.67	89.6	
3	$CH_3CH_2CH_2$	0.42	1000	0.4809	1.10	94.9	
		0.21	2000	0.3611	1.65	95.0	266.7
		0.105	4000	0.2151	1.97	91.0	
2	CH_2=$CHCH_2CH_2$	0.42	1000	0.5620	1.29	94.2	
		0.21	2000	0.5836	2.67	96.8	266.4
		0.105	4000	0.3637	3.83	95.6	
4	$CH_3CH_2CH_2CH_2$	0.42	1000	0.5793	1.33	94.6	
		0.21	2000	0.4165	1.91	96.1	265.6
		0.105	4000	0.2143	1.96	93.5	
5	H	0.42	1000	0.5318	1.22	91.4	
		0.21	2000	0.5519	2.53	94.5	257.9
		0.105	4000	0.2378	2.18	89.7	

[a] Polymerization conditions: 50 °C for 0.5 h; styrene: = 2 ml; V_{total} = 12 ml.
[b] g PS (mol Ti mol S h)$^{-1}$.
[c] Grams of 2-butanone insoluble polymer/gram of bulk polymer.
[d] Melting temperature of s-PS.

The dependence of activity and syndiotacticity on polymerization temperature is summarized in Table 2.

From the results in Tables 1 and 2, the maximum polymerization activities of complexes **1** to **4** were obtained at 75 °C. A higher temperature (90 °C) led to a decrease in the activities and syndiotacticities of polystyrenes due to decomposition of the active species[25,43]. In the temperature range 25 to 90 °C, complex **1** exhibited the lowest activity and syndiotacticity, and complex **2** showed the highest activity and syndiotacticity.

Table 3 summarizes the dependence of the polymerization activity on the polymerization time. The maximum activity was reached after 5 min and thereafter it decreased; it is clear that complexes **2** and **4** showed higher activities than complexes **1** and **3** respectively. The difference in the activities between complex **1** and complex **2** was much larger than that between complex **3** and complex **4**. This is another hint that the C=C bond of the allyl group in complex **1** might coordinate strongly to titanium(III), and block one coordination site for a short period of time. For the 1-RIndTiCl$_3$/MAO system[32] they exhibited the opposite trend: their polymerization activities increased in the order n-Pr > CH$_2$=CHCH$_2$CH$_2$ > CH$_2$=CHCH$_2$ > n-Bu.

Table 2. Influence of the temperature of polymerization catalyzed by RCpTiCl$_3$/MAO systems[a]

Catalyst	R	T_P (°C)	Yield (g)	Activity[b] (×10^7)	s-PS[c] (%)
1	CH$_2$=CHCH$_2$	25	0.0998	0.46	87.9
		75	0.3898	1.79	83.3
		100	0.3751	1.72	57.8
3	CH$_3$CH$_2$CH$_2$	25	0.2212	1.01	91.1
		75	0.5484	2.51	91.8
		100	0.4860	2.23	67.0
2	CH$_2$=CHCH$_2$CH$_2$	25	0.2514	1.15	94.4
		75	0.6127	2.81	90.7
		100	0.5087	2.33	72.8
4	CH$_3$CH$_2$CH$_2$CH$_2$	25	0.1758	0.81	92.9
		75	0.4830	2.21	92.4
		100	0.5904	2.71	63.4
5	H	25	0.2743	1.26	92.5
		75	0.5390	2.47	74.2
		100	0.5223	2.39	47.1

[a] Polymerization conditions: [Ti] = 0.21 mM; Al/Ti = 2000; T_P = 0.5 h; styrene: 2 ml, V_{total} = 12 ml.
[b] g PS (mol Ti mol S h)$^{-1}$.
[c] Grams of 2-butanone insoluble polymer/gram of bulk polymer.

Table 3. Dependence of the polymerization activity on the polymerization time with RCpTiCl$_3$[a]

	Activity[b] (×10^7)			
t_P(min)	**1**	**2**	**3**	**4**
5	1.83	6.71	3.76	5.43
10	1.68	5.42	3.24	3.76
20	1.33	3.65	2.08	2.59
30	1.07	2.67	1.65	1.91

[a] Polymerization conditions: [Ti] = 0.21 mM; Al/Ti = 2000; T_P = 50 °C; styrene: 2 ml, V_{total} = 12 ml.
[b] g PS (mol Ti mol S h)$^{-1}$.

The influence of the concentration of MAO, (triisobutylaluminum TIBA) and (diisobutylaluminum hydride DIBAH) on the activity with complex **1** is summarized in Table 4.

From run 1 to run 5, the activity increased with increasing molar ratio of MAO to titanium, because the amount of cationic titanium(III) species measured by electron spin resonance increases with increasing concentration of MAO[44].

TIBA and DIBAH are often added into the MAO co-catalyst system in industry in order to decrease the concentration of MAO, because they were found to be the scavenger of impurities in styrene and to increase the syndiotacticity of the polymer.[45–49] Moreover, the costs of TIBA and DIBAH are much lower than that of MAO. Comparing run 1 with run 4, run 2 with run 5 and run 6 with run 7, it is clear that the activity increased with increasing concentration of TIBA. Addition of DIBAH into the catalyst system increased the activity at the lower molar ratio of TIBA to titanium (run 4 and run 6); however, at the higher molar ratio of TIBA to titanium (run 1 and run 7), addition of DIBAH decreased the activity. This may be caused by the reducing ability of DIBAH, which is stronger than that of TIBA, and some titanium(III) may be further reduced to titanium(II) or titanium(I).

EXPERIMENTAL

Measurements

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by distillation over sodium benzophenone

Table 4. Influences of MAO, DIBAH, and TIBA on the activity of styrene polymerization[a]

	Molar ratio					Activity[b](×10^5)
Run	Cat	DIBAH	TIBA	MAO	Styrene	
1	1	25	200	100	150 000	1.87
2	1	25	200	150	150 000	2.62
3	1	25	100	75	150 000	1.22
4	1	25	100	100	150 000	1.33
5	1	25	100	150	150 000	1.96
6	1	0	100	100	150 000	0.84
7	1	0	200	100	150 000	2.61

[a] Polymerization condition: complex **1**; 50 °C; styrene: = 35 ml; no additional solvent; 1 h.
[b] g PS (mol Ti mol S h)$^{-1}$.

(diethyl ether, tetrahydrofuran(THF), toluene and *n*-hexane) and CaH_2 (dichloromethane).

MAO, TIBA and DIBAH were produced by Witco GmbH. Styrene was purified by washing several times with dilute NaOH solution, dried over anhydrous $CaCl_2$, vacuum distillation from CaH_2 and stored at −20 °C in darkness. $CH_2{=}CHCH_2CpSiMe_3$, $CH_2{=}CHCH_2CH_2CpH$ and $CH_3CH_2CH_2CH_2CpTiCl_3$ were synthesized by using a published method[50–52].

Mass spectra were measured on an HP5989A spectrometer. IR spectra were recorded on a Nicolet FTIR 5SXC spectrometer. ^1H NMR was measured on a Varian GRMINI-300 spectrometer using tetramethylsilane (TMS) as an internal standard. Elemental analyses were performed by Shanghai Institute of Organic Chemistry. Melting points were uncorrected.

Synthesis

$CH_2{=}CHCH_2CpTiCl_3$ (1)

A CH_2Cl_2 (10 ml) solution of 3.76 g (0.021 mol) $CH_2{=}CHCH_2CpSiMe_3$ was added slowly to a CH_2Cl_2 (50 ml) solution of 2.33 ml (0.021 mol) $TiCl_4$ at −70 °C. The solution was allowed to warm to room temperature and stirred overnight. The solvent was removed under vacuum. The residue was extracted into hot *n*-hexane (70 ml) and filtered. On cooling to −30 °C, the product was obtained as yellow needle crystals; yield, 3.48 g, 64%; m.p. = 54–56 °C. ^1H NMR ($CDCl_3$): δ 3.63 (d, $J = 6.6$ Hz, 2H, CH_2), 5.15–5.24 (m, 2H, $CH_2{=}$), 5.89–6.03 (m, 1H, $CH{=}$), 6.85 (t, $J = 2.7$ Hz, 2H, Cp), 6.96 (t, $J = 2.7$ Hz, 2H, Cp). IR (KBr): ν 3098m, 2975w, 2901w, 2842w, 1838w, 1640m ($\nu_{C=C}$), 1488m, 1426m, 1038m, 995m, 926m, 834s, 775s, 716m. MS (*m/z*): 223 (34) $[M^+ - Cl]$, 188 (45) $[M^+ - 2Cl]$, 105 (54) $[C_3H_5Cp^+]$. Anal. Found: C, 37.06; H, 3.68. Calc. for $C_8H_9Cl_3Ti$: C, 37.04; H, 3.50%.

$CH_2{=}CHCH_2CH_2CpSiMe_3$

A solution of 42.3 ml (0.0656 mol) of *n*-BuLi (1.55 M) was added dropwise to a THF (100 ml) solution of 7.87 g (0.0656 mol) of 3-butenyl-cyclopentadiene at 0 °C. The solution was allowed to equilibrate at room temperature and stirred for 3 h. Then 8.4 ml (0.0656 mol) of chlorotrimethylsilane was added dropwise to the stirred solution at room temperature, and the mixture was stirred for 2 h. The solution was filtered and the solvent was removed under vacuum. The residual oil was distilled at 83–85 °C/9 mmHg to give 9.65 g (77%) pale yellow oil. ^1H NMR ($CDCl_3$): δ 0.02–0.17 (m, 9H, $Si(CH_3)_3$), 2.30–2.36 (m, 2H, CH_2), 2.53 (t, $J = 7.2$ Hz, 2H, CH_2), 3.28 (s, 1H, Cp), 4.97–5.10 (m, 2H, $CH_2{=}$), 5.84–5.97 (m, 1H, $CH{=}$), 6.13–6.50 (m, 3H, Cp).

$CH_2{=}CHCH_2CH_2CpTiCl_3$ (2)

The same procedure as described for **1** was used. The $CH_2{=}CHCH_2CH_2CpSiMe_3$ (2.49 g, 0.013 mol) and $TiCl_4$ (1.43 ml, 0.013 mol) were used to give 1.51 g (42%) of orange–red flat crystals, m.p. = 34–36 °C. ^1H NMR ($CDCl_3$): δ 2.40–2.48 (m, 2H, CH_2), 2.98 (t, $J = 7.9$ Hz, 2H, CH_2), 5.04–5.10 (m, 2H, $CH_2{=}$), 5.77–5.90 (m, 1H, $CH{=}$), 6.86 (t, $J = 2.7$ Hz, 2H, Cp), 6.95 (t, $J = 2.7$ Hz, 2H, Cp). IR (KBr): ν 3100m, 2965m, 2930m, 2845m, 1834w, 1641m ($\nu_{C=C}$), 1488m, 1441m, 1422m, 1046m, 996m, 922m, 844s, 775m. MS (*m/z*): 237 (86) $[M^+ - Cl]$, 202 (75) $[M^+ - 2Cl]$, 78 (100) $[CH_2Cp^+]$. Anal. Found: C, 39.73; H, 4.09. Calc. for $C_9H_{11}Cl_3Ti$: C, 39.53; H, 4.06%.

$CH_3CH_2CH_2CpTiCl_3$ (3)

The same procedure as described for **1** was used. The $CH_3CH_2CH_2CpSiMe_3$ (1.30 g, 0.00722 mol) and $TiCl_4$ (0.8 ml, 0.00722 mol) were used to give 0.956 g (51%) of yellow needle crystals. ^1H NMR ($CDCl_3$): δ 1.01 (t, $J = 7.3$ Hz, 3H, CH_3), 1.67–1.75 (m, 2H, CH_2), 2.84 (t, $J = 7.7$ Hz, 2H, CH_2), 6.86 (t, $J = 2.7$ Hz, 2H, Cp), 6.94 (t, $J = 2.7$ Hz, 2H, Cp). IR (KBr): ν 3102w, 2960m, 2932w, 2871w, 1489w, 1461w, 1379w, 1056w, 1038w, 937w, 856m, 824s, 801s, 708m, 663m, 591m. MS (*m/z*): 260 (3) $[M^+]$, 225 (8) $[M^+ - Cl]$, 224 (18) $[M^+ - HCl]$, 190 (35) $[M^+ - 2Cl]$, 188 (100) $[M^+ - 2HCl]$, 107 (5) $[C_3H_7Cp^+]$, 79 (45) $[CH_3Cp^+]$, 78 (22) $[CH_2Cp^+]$. Anal. Found: C, 36.68; H, 4.19. Calc. for $C_8H_{11}Cl_3Ti$: C, 36.76; H, 4.24%.

Polymerization procedure

Polymerization was conducted in small ampoules baked under vacuum and flushed with argon several times. Styrene, toluene, DIBAH, TIBA and MAO were sequentially injected, and the catalyst precursor in toluene was then added. The bottle was immediately placed in an oil bath at the desired polymerization temperature. After 1 h, the polymerization was quenched with 10% HCl in ethanol, filtered, and dried under vacuum at 80 °C for 24 h to a constant weight. The melting temperature of the polymers was recorded on a DSC Universal V2.3C TA instrument.

CONCLUSION

We have prepared three new substituted cyclopentadienyl titanium trichlorides. The catalyst activities of syndiotactic polymerization of styrene decreased in the order $CH_2{=}CHCH_2CH_2CpTiCl_3$ (**2**) $> CpTiCl_3 > CH_3CH_2CH_2CH_2CpTiCl_3$ (**4**) $> CH_3CH_2CH_2CpTiCl_3$ (**3**) $> CH_2{=}CHCH_2CpTiCl_3$ (**1**). Introduction of an alkenyl or *n*-alkyl group into the Cp-ligand increased the melting points of polystyrenes and the stabilities of catalysts; this was reflected in the higher melting points of polymers and the higher temperature of the maximum activities compared with $CpTiCl_3$. The difference in the activities between complex **1** and complex **2** was much larger than that between complex **3** and complex **4**, and complex **1** showed the lowest activity and syndiotacticity; this indicated that the C=C bond of the allyl group might coordinate strongly to the active center, which interfered with the coordination and the insertion of styrene. Compared with the *n*-butyl group of complex **4**, the 3-butenyl group of complex **2** may be beneficial in stabilizing the active center while not hindering the coordination and the insertion of the monomer. With complex **1**, the dependence of the activity on the concentration of MAO, TIBA and DIBAH was investigated. It was observed that the activity increased with increasing concentration of MAO or TIBA. Addition of DIBAH into the catalyst system increased the activity at the lower molar ratio of TIBA to titanium; however, at the higher molar ratio of TIBA to titanium the addition of DIBAH decreased the activity.

Acknowledgements

Financial support was subsidized by the Special Funds for Major State Basic Research Projects (G1999064801). We thank BASF-AG (Ludwigshafen) for generous gifts of MAO and Dr M. Geprägs (BASF-AG) for valuable technical advice.

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