

Synthesis and styrene polymerization behavior of new titanium complexes $\text{Cp}^*\text{TiCl}(\text{OCHRCH}_2\text{NAr})$

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Abstract

A series of titanium complexes $\text{Cp}^*\text{TiCl}(\text{OCHRCH}_2\text{NAr})$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{R} = \text{H}$, $\text{Ar} = \text{phenyl}$ (**2a**); $\text{R} = \text{H}$, $\text{Ar} = 2,6\text{-dimethylphenyl}$ (**2b**); $\text{R} = \text{Me}$, $\text{Ar} = \text{phenyl}$ (**2c**); $\text{R} = \text{Me}$, $\text{Ar} = 2,6\text{-dimethylphenyl}$ (**2d**)) was prepared by the reaction of corresponding 2-phenylamino-ethanol derivatives with Cp^*TiCl_3 in the presence of excessive triethylamine. All the titanium complexes display higher catalytic activity towards the syndiospecific polymerization of styrene in the presence of modified methylaluminoxane (MMAO) as a cocatalyst, yielding higher molecular weight polystyrenes with higher syndiotacticities and melting temperatures (T_m) than their mother complex Cp^*TiCl_3 . When 2-(2,6-diisopropyl-phenylamino)-ethanol was reacted with Cp^*TiCl_3 , an unexpected monodentate complex $\text{Cp}^*\text{TiCl}_2(\text{OCH}_2\text{CH}_2\text{NHC}_6\text{H}_3^i\text{Pr}_2\text{-}2,6)$ **3** was obtained. The complex **3** displays relative low catalytic activity towards styrene polymerization, but produces higher molecular weight polystyrene with higher syndiotacticities.

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Keywords: Titanium complex; Catalyst; Styrene; Modified methylaluminoxane; Syndiospecific polymerization; Polystyrene

1. Introduction

Olefin polymerization by homogeneous catalysis has become one of the most attractive subjects in the field of both organometallic chemistry and catalysis. The use of titanium complex/methylaluminoxane catalyst system in the first preparation of syndiotactic polystyrene (sPS) by Ishihara and his colleagues has impelled an active search for new types of sPS catalysts [1–4]. A wide variety of catalytic systems based on titanium complexes have been reported in [5–12]. Most of the extensive work on sPS catalysts has been focused on the modification of the η^5 ligand system. In addition, the σ -donor X (X = halogen, alkoxy or hydrocarbyl) ligand has been also found to affect both catalytic activities and polymer properties. For instance, by application of alkoxy ligand substi-

tuted complexes, e.g. $\text{CpTiCl}_2(\text{OR})$ or $\text{Cp}^*\text{Ti}(\text{OR})_3$, in place of chlorinated counterparts [13–15], some research groups have found that the former have much higher activity than the latter [16–23].

In 1998, Doherty et al. reported that the mixed-ligand titanium complexes $\text{CpTi}(\text{NC}_5\text{H}_4(\text{CR}_2\text{O}))\text{Cl}_2$ ($\text{NC}_5\text{H}_4(\text{CR}_2\text{O}) =$ bidentate pyridylalkoxide ligand) and $\text{CpTi}(\text{ONO})\text{Cl}_2$ ($\text{ONO} =$ tridentate *N*-alkoxy- β -ketoiminate ligand) are more active towards ethylene polymerization than their mother complex CpTiCl_3 [24]. Qian and coworkers reported that two kinds of titanium complexes with mono-Cp and Schiff base ligands display improved catalytic activities for olefin polymerization in comparison with CpTiCl_3 [25]. Xu et al. showed that the complexes $\text{CpTi}(\text{dbm})_x\text{Cl}_{3-x}$ ($\text{dbm} = 1,3\text{-diphenylpropane-}1,3\text{-dione}$ ligand) [26], $\text{CpTi}[\text{O},\text{N}]\text{Cl}_2$ containing 8-hydroxy-quinoline ligand [27], and $\text{CpTi}[\text{O},\text{O}]\text{Cl}$ bearing bisphenoxy ligands [28] can act as active catalysts for ethylene polymerization in the presence

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MAO. We deduce that some mixed-ligand titanium complexes $\text{Cp}^*(\text{L})\text{TiCl}_x$ (Cp^* = pentamethylcyclopentadienyl, L = multidentate ligands, $x=0-3$) could display higher activities for styrene polymerization than their mother complex Cp^*TiCl_3 .

Herein we report the synthesis, characterization and styrene polymerization behavior of a series of new titanium complexes $\text{Cp}^*\text{TiCl}(\text{OCHRCH}_2\text{NAr})$ in the presence of MMAO as a cocatalyst, and compare their performance with that of their mother complex Cp^*TiCl_3 .

2. Experimental

2.1. General procedures and materials

All work involving air and moisture sensitive compounds was carried out using standard Schlenk techniques. Electron impact mass spectra were obtained with a VG Auto Spectrometer. Elemental analyses were performed with an EA-1106 spectrometer. The NMR data of ligands and complexes were obtained on a Bruker 300 MHz spectrometer at ambient temperature, with CDCl_3 as solvent and TMS as internal standard. The NMR data of the polystyrenes were obtained on a Varian Unity 400 MHz spectrometer at 100 °C with 1,1,2,2-tetrachloroethane- d_2 as the solvent and TMS as internal standard. The pulse interval was 7.93 s, the acquisition time was 0.33 s, the pulse angle was 90°, and the number of transients accumulated was ca. 5000. The molecular weights and the polydispersity indices of the polymer samples were determined at 150 °C by a PL-GPC 220 type high temperature chromatograph equipped with three PLgel 10 μm Mixed-B LS type columns. 1,2,4-Trichlorobenzene (TCB) was employed as the solvent at a flow rate of 1.0 mL/min. The calibration was made by polystyrene standard EasiCal PS-1 (PL Ltd.).

Toluene was dried over sodium with dibenzophenone as indicator. Dichloromethane and triethylamine were refluxed over calcium hydride for two weeks before use. CDCl_3 was obtained from Aldrich and dried over CaH_2 , vacuum-transferred, degassed by repeated freeze-pump-thaw cycles, and stored over activated molecular sieves (4A). The aniline, 2,6-dimethylaniline, 2,6-diisopropylaniline and 1,1,2,2-tetrachloroethane- d_2 were obtained from Acros and purified by distillation before use. Modified methylaluminoxane (MMAO, 7 wt.% Aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. Styrene was distilled from CaH_2 and stored in a refrigerator. Pentamethylcyclopentadienyl titanium trichloride were obtained from Strem and used without purification. 2-phenylamino-ethanol, 2-(2,6-dimethyl-phenylamino)-ethanol, 2-(2,6-diisopropyl-phenylamino)-ethanol, 1-phenylamino-propan-2-ol, and 1-(2,6-dimethyl-phenylamino)-propan-2-ol were synthesized in good yields according to the published literature procedures [29].

2.2. Synthesis of complexes

To a solution of 2-phenylamino-ethanol (0.686 g, 5.0 mmol) and triethylamine (1.4 mL) in 40 mL of CH_2Cl_2 was added dropwise a reddish solution of Cp^*TiCl_3 (1.45 g, 5.0 mmol) in 40 mL of CH_2Cl_2 under stirring and at -78°C . The reaction mixture was warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under reduced pressure, was redissolved in toluene, and the resulting mixture was filtered through a Celite bed. The removal of solvent from the orange filtrate afforded the titanium complex ($\text{Cp}^*\text{TiCl}(\text{OCH}_2\text{CH}_2\text{NC}_6\text{H}_5)$) **2a** in 88% yield (1.55 g). The other complexes were prepared by a similar procedure in similar yields.

2a ($\text{Cp}^*\text{TiCl}(\text{OCH}_2\text{CH}_2\text{NC}_6\text{H}_5)$): ^1H NMR (CDCl_3): δ 7.32–7.13 (m, 5H, C_6H_5), 3.92–3.88 (t, 2H, OCH_2), 3.38–3.35 (t, 2H, NCH_2), 2.05 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR (CDCl_3): δ 147.2, 131.7, 129.2, 128.2 (Ph), 113.4 (C_5Me_5), 74.71 (OCH_2), 46.65 (NCH_2), 12.32 ($\text{C}_5(\text{CH}_3)_5$). EIMS: m/z (relative intensity): 352 ($[\text{M}^+]$, 44), 322 ($[\text{M}^+ - \text{CH}_2\text{O}]$, 100), 217 ($[\text{M}^+ - \text{Cp}^*]$, 50), 216 ($[\text{M}^+ - \text{ArNCH}_2\text{CH}_2\text{O}]$, 40). Anal. Calc. for $\text{C}_{18}\text{H}_{24}\text{ClNO}$: C, 61.12; H, 6.84; N, 3.96%. Found: C, 61.26; H, 6.78; N, 4.01%.

2b ($\text{Cp}^*\text{TiCl}(\text{OCH}_2\text{CH}_2\text{NC}_6\text{H}_3(\text{CH}_3)_2)$) (85%): ^1H NMR (CDCl_3): δ 7.28–6.99 (m, 3H, C_6H_3), 4.20–4.17 (t, 2H, OCH_2), 3.43–3.40 (t, 2H, NCH_2), 2.05 (s, 6H, PhCH_3), 2.08 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR (CDCl_3): δ 142.5, 132.7, 130.6, 129.6 (Ph), 128.2 ($\text{C}_5(\text{CH}_3)_5$), 58.26 (OCH_2), 46.20 (NCH_2), 18.95 (PhCH_3), 12.75 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calc. for $\text{C}_{20}\text{H}_{28}\text{ClNO}$: C, 62.92; H, 7.39; N, 3.67. Found: C, 63.09; H, 7.35; N, 3.71%.

2c ($\text{Cp}^*\text{TiCl}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{NC}_6\text{H}_5)$) (82%): ^1H NMR (CDCl_3): δ 7.30–7.09 (m, 5H, C_6H_5), 4.19–4.15 (m, 1H, OCH), 3.28–3.23 (d, 2H, NCH_2), 2.12 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.16 (d, 3H, CHCH_3). ^{13}C NMR (CDCl_3): δ 146.5, 132.7, 126.9, 125.1 (Ph), 117.8 (C_5Me_5), 76.58 (OCH), 49.66 (NCH_2), 22.5 (CHCH_3), 12.58 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calc. for $\text{C}_{19}\text{H}_{26}\text{ClNO}$: C, 62.07; H, 7.08; N, 3.81. Found: C, 62.19; H, 7.13; N, 3.89%.

2d ($\text{Cp}^*\text{TiCl}(\text{OCH}(\text{CH}_3)\text{CH}_2\text{NC}_6\text{H}_3(\text{CH}_3)_2)$) (79%): ^1H NMR (CDCl_3): δ 7.18–7.12 (m, 3H, C_6H_3), 4.61–4.59 (m, 1H, OCH), 3.44–3.40 (d, 2H, NCH_2), 2.55 (s, 6H, PhCH_3), 2.06 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.16 (d, 3H, CHCH_3). ^{13}C NMR (CDCl_3): δ 147.7, 132.5, 129.1, 127.1 (Ph), 113.9 (C_5Me_5), 75.4 (OCH), 55.5 (NCH_2), 22.9 (PhCH_3), 22.5 (CHCH_3), 13.2 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calc. for $\text{C}_{21}\text{H}_{30}\text{ClNO}$: C, 63.73; H, 7.63; N, 3.54. Found: C, 63.58; H, 7.58; N, 3.58%.

3 ($\text{Cp}^*\text{TiCl}_2(\text{OCH}_2\text{CH}_2\text{NHC}_6\text{H}_3(\text{Pr})_2)$) (82%): ^1H NMR (CDCl_3): δ 7.12–7.05 (m, 3H, Ph-H), 4.80 (t, 2H, OCH_2), 4.16 (s, 1H, NH), 3.32 (m, 2H, CHMe_2), 3.16–3.09 (t, 2H, NCH_2), 2.26 (s, 15H, $\text{C}_5(\text{CH}_3)_5$), 1.23 (d, 12H, $\text{CH}(\text{CH}_3)_2$). ^{13}C NMR (CDCl_3): δ 143.5, 132.0, 129.4, 125.7 (Ph), 123.9 (C_5Me_5), 59.2 (OCH_2), 54.2 (NCH_2), 28.3 (CHMe_2), 25.1 ($\text{CH}(\text{CH}_3)_2$), 13.11 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calc. for $\text{C}_{24}\text{H}_{37}\text{Cl}_2\text{NO}$: C, 60.77; H, 7.86; N, 2.95. Found: C, 60.58; H, 7.83; N, 2.99%.

2.3. Polymerization procedure

Polymerization was carried out in toluene in a 150 mL glass reactor equipped with a mechanical stirrer. Toluene, styrene, and the solution of titanium complex were introduced into the nitrogen-purged reactor and stirred vigorously (600 rpm) at the desired temperature. The reaction was started by the addition of an MMAO solution. After 10 min, reaction was terminated by the addition of 100 mL of acidic ethanol (ethanol/HCl_{conc.} = 20/1). The resulting precipitated polymer was washed three times with 500 mL portions of methanol and dried in vacuo at 70 °C for 24 h. The polymer was extracted with refluxing 2-butanone for 12 h in order to determine the syndiotacticity of the polymer obtained by measuring of ¹³C NMR spectra at 100 °C in 1,1,2,2-tetrachloroethane-*d*₂.

3. Results and discussion

3.1. Synthesis and characterization of titanium complexes

A general synthetic route for new titanium complexes Cp*TiCl(OCHRCH₂NAr) used in this study is shown in Scheme 1. Complexes **2a–d** were obtained in good yields (**2a**, 88%; **2b**, 85%; **2c**, 82%; **2d**, 79%) by the reaction of corresponding 2-phenylamino-ethanol derivative with Cp*TiCl₃ in the presence of excessive triethylamine. Attempted use of dilithiated species instead of neutral 2-phenylamino-ethanol derivatives in toluene or diethyl ether was not successful and a mixture of several unidentified compounds was obtained, suggesting that mild reaction condition of HCl elimination is essential and required for the synthesis of titanium complexes Cp*TiCl(OCHRCH₂NAr).

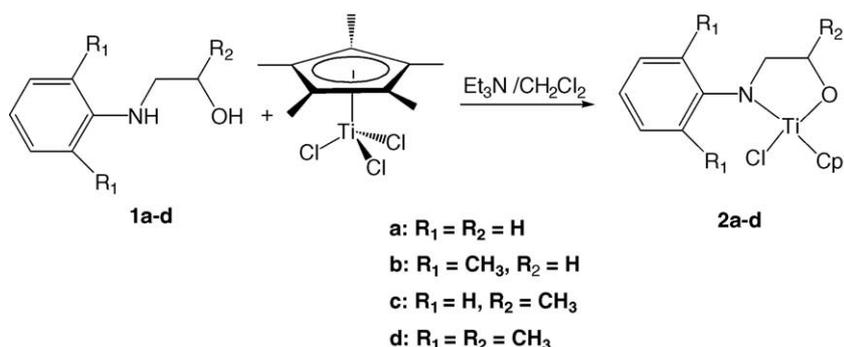
Owing to the failure in obtaining single crystals for **2a–d**, their structural characters were established by NMR spectroscopy, EI mass spectroscopy, and elemental analyses. The ¹H and ¹³C NMR of **2a–d** show the presence of only one pure compound. The stoichiometry of the reaction was ascertained from the ratio of ¹H NMR. In comparison with the free 2-phenylamino-ethanol derivatives, all signals in the ¹H

and ¹³C NMR spectra of the complexes **2a–d** are shifted to the downfield, which is a consequence of the high Lewis acidity of titanium. In the ¹H NMR spectra, the resonance signals of group OCH₂ shifted downfield by 0.8–1.1 ppm versus the free ligand, while only a small downfield shift by 0.3–0.5 ppm was observed for the CH₂N resonance. This suggests that a strong bond formed between the titanium atom and oxygen atom of the ligand, and a weak bond formed between the titanium and the nitrogen atom of the ligand. The NMR signals were sharp, and variable-temperature studies showed no evidence of inter- or intramolecular ligand exchange at ambient temperature. In the absence of X-ray structure determination of the complexes **2a–d**, it is difficult to clarify whether **2a–d** are monomeric, dimeric or polymeric species. However, we tentatively suggest that **2a–d** should exist most likely as monomeric species in solution, because the NMR spectra of the complexes **2a–d** are sharp, they have some volatile nature, and the EI mass spectra exhibit molecular peaks for the corresponding complexes.

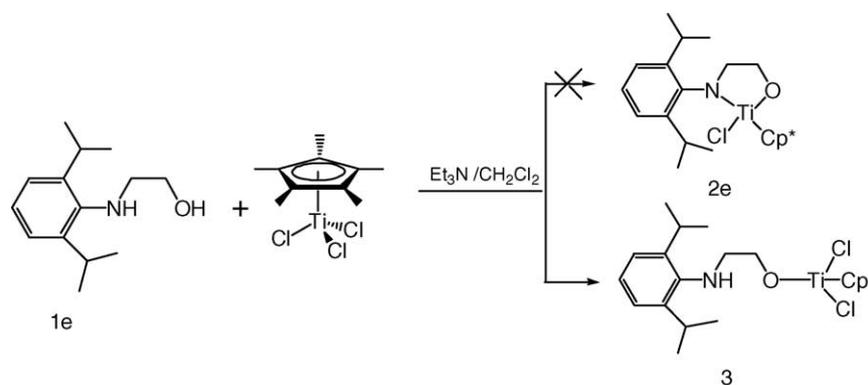
Attempts to prepare Cp*TiCl[OCH₂CH₂N(2,6-*i*Pr₂Ph)] **2e** via the approach aforementioned were unsuccessful, giving acyclic complex **3** in which the nitrogen atom is not found coordinated with titanium atom, as shown in Scheme 2. The reason why the complex **2e** cannot be formed is that there is a steric hindrance between bulky isopropyl and pentamethylcyclopentadienyl groups. Crystal structure determination confirms the deduction aforementioned. The molecular structure of **3** is shown in Fig. 1. The data collection and refinement data of the analysis are summarized in Table 1.

3.2. Catalysis

Polymerizations of styrene with **2a–d**, **3**/MMAO catalytic systems were performed in toluene under various conditions. In order to assess the significance of the observed activity values, we also carried out the polymerization experiments by using Cp*TiCl₃/MMAO catalytic system under the same polymerization conditions. The polymerization data, summarized in Table 2, reveal that the **2a–d**/MMAO catalytic systems are more efficient in producing highly syndiotactic polystyrene in terms of activity, conversion, and stereospecificity at all the polymerization temperatures.



Scheme 1.



Scheme 2.

Catalyst activities and polymer yields as well as molecular weights depend significantly on the reaction conditions. The variation of the ratio of MMAO/2a, which is expressed here as Al/Ti molar ratio, showed considerable effects on polymer yield, polymer molecular weights and catalyst activities. As

shown in Fig. 2, the activity of the complex 2a rapidly increases at first with an increase in the Al/Ti molar ratio, and then decreases gradually. The optimal Al/Ti molar ratio is ca. 1100/1. Contrarily, the molecular weight of polymer gradually decreases in line with an increase in the Al/Ti molar ratio.

Considerable effects of the molar ratio of monomer to catalyst on the catalyst activities and the molecular weight of polymer were also observed. An increase in the styrene/Ti molar ratio, which also means an increase in the monomer concentration (the reaction volume was kept constant), first

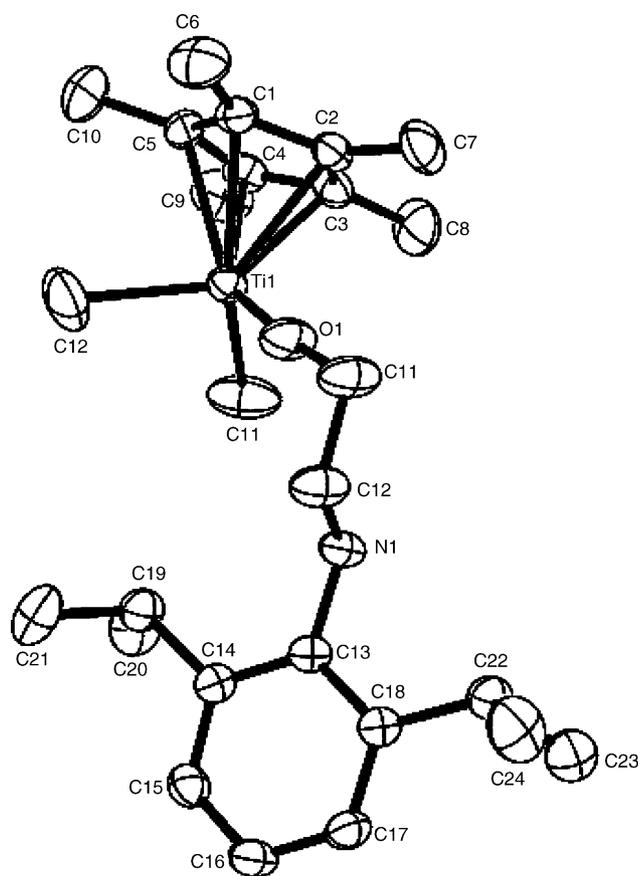


Fig. 1. ORTEP plot of the molecular structure of the titanium complex 3. Displacement ellipsoids are drawn at the 30% probability level. Hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Ti(1)–O(1), 1.7493(17); Ti(1)–Cl(1), 2.2588(9); Ti(1)–Cl(2), 2.2553(9); Ti(1)–C(1), 2.330(2); Ti(1)–C(4), 2.383(2); Ti(1)–C(5), 2.385(2); O(1)–C(11), 1.417(3); C(1)–C(2), 1.409(3); C(1)–C(5), 1.426(3); C(2)–C(3), 1.403(3); C(3)–C(4), 1.396(4); C(4)–C(5), 1.396(4); O(1)–Ti(1)–Cl(1), 101.82(8); O(1)–Ti(1)–Cl(2), 101.87(8); Cl(2)–Ti(1)–Cl(1), 102.60(5).

Table 1

Crystal data and structure refinement of the titanium complex 3

Empirical formula	$\text{C}_{24}\text{H}_{37}\text{Cl}_2\text{NOTi}$
Formula mass	474.35
Crystal size (mm)	$0.55 \times 0.52 \times 0.10$
Crystal system	Monoclinic
Space group	$P2(1)/n$
a (Å)	8.5183 (2)
b (Å)	15.8836 (5)
c (Å)	19.4969 (7)
α (°)	90
β (°)	92.3170 (10)
γ (°)	90
Volume (Å ³)	2635.80 (14)
Z	4
ρ_{calc} (Mg cm ⁻³)	1.195
Absorption coefficient (mm ⁻¹)	0.541
$F(000)$	1008
θ range for data collected (°)	2.45–27.48
Limiting indices	$0 \leq h \leq 11, 0 \leq k \leq 20,$ $-25 \leq l \leq 25$
Reflections collected/unique	12710/5860
R_{int}	0.0277
Completeness to θ	27.48–97.1%
Maximum and minimum transmission	0.9474 and 0.7558
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	5860/0/287
Goodness-of-fit on F^2	0.870
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0455, wR_2 = 0.1195$
R indices (all data)	$R_1 = 0.0859, wR_2 = 0.1279$
Largest different peak and hole	0.512 and -0.304 eÅ^{-3}

Table 2
Polymerization results of styrene with titanium complexes/MMAO^a

Catalyst	T_p (°C)	PS (g)	Activity ^b	Conversion (%)	sPS ^c (%)	SI ^d (%)	\bar{M}_w ^e (kg/mol)	\bar{M}_w/\bar{M}_n
Cp*TiCl ₃	30	0.88	0.60	19.3	96.9	97.7	231	1.71
	50	2.62	1.80	57.6	96.5	96.0	197	1.73
	70	3.00	2.06	65.9	95.2	95.4	182	2.08
2a	30	0.89	0.61	19.6	99.2	98.9	247	2.53
	50	2.68	1.84	58.9	99.0	98.5	222	2.16
	70	3.27	2.25	72.0	98.5	98.6	196	2.09
2b	30	0.93	0.64	20.5	98.9	99.1	253	2.45
	50	2.72	1.87	59.9	98.8	98.7	226	2.10
	70	3.35	2.30	73.7	98.2	99.0	200	1.98
2c	30	0.99	0.68	21.8	99.1	99.2	268	2.37
	50	2.79	1.92	61.3	99.2	99.1	231	2.03
	70	3.45	2.37	75.9	98.3	98.5	202	2.01
2d	30	1.17	0.81	25.8	98.9	99.3	270	2.29
	50	2.82	1.94	62.1	98.7	98.9	235	1.99
	70	3.54	2.43	77.9	98.1	98.7	204	1.93
3	30	0.44	0.30	9.7	98.5	98.7	315	2.35
	50	1.30	0.89	28.6	98.4	98.2	293	2.19
	70	2.89	1.98	63.6	97.9	98.3	272	2.02

^a Polymerization condition: 20 μ mol catalyst, Al/Ti = 1000 (molar ratio), styrene/Ti = 2200 (molar ratio), $V_{\text{total}} = 100$ mL, polymerization for 10 min.

^b Activity = 10^4 kg sPS/mol_{Ti} mol_{St} h.

^c sPS% = (g of polymer soluble in 2-butanone)/(g of total polymer) \times 100%.

^d SI = syndiotacticity (2-butanone insoluble portion whose tacticity established by ¹³C NMR in 1,1,2,2-tetra-chloroethane-*d*₂).

^e Determined by GPC.

caused a dramatic increase in the catalytic activity of the complex **2a** and then a rapid decrease. The optimum molar ratio of monomer to catalyst is ca. 2000, as shown in Fig. 3. Contrarily, the molecular weights of polymers increase in the range of the conditions studied.

It is very interesting to note that reaction temperature also affects considerably the activities of catalysts and the molecular weights of polymers (see Table 2). With increase of reaction temperature, the catalyst activity of the complex **2a** rapidly increases at first, and then decreases slowly, as shown in Fig. 4. The optimum reaction temperature is ca.

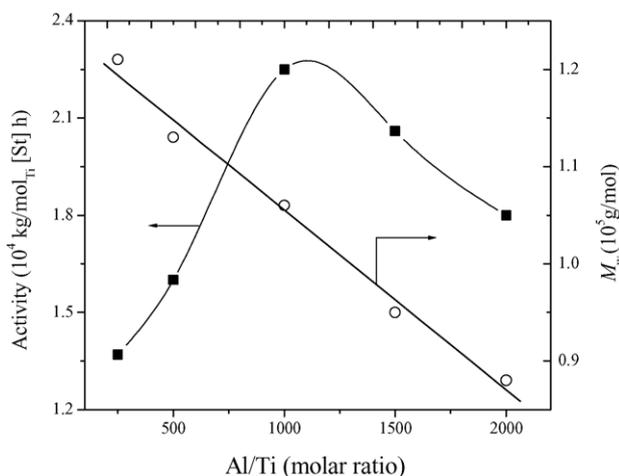


Fig. 2. Plot of activity and \bar{M}_w vs. Al/Ti molar ratio. A 20 μ mol **2a**, styrene/Ti = 2200 (molar ratio), $V_{\text{total}} = 100$ mL, polymerization reaction at 70 °C for 10 min.

70 °C. In contrast, the molecular weights of the polymer obtained decrease monotonously with reaction temperature. The stereospecificities of the polymers obtained exhibit the similar reaction temperature dependency. As many homogeneous half-sandwich metallocene catalysts based on tridentate ligands [15,30], **2a–d**/MMAO systems also show a slightly low syndiotacticity values with an increase in reaction temperature.

The data, listed in Table 2, indicate clearly that the structures of the titanium complexes considerably affect their performance. It is well known that steric effect could control the deactivation of the catalysts for olefin polymerization, the chain transfer such as β -hydride elimination, and chain termination [31–34]. As a result, the catalytic activities, polymer yields and molecular weights increase gradually from **2a** through **2b** and **2c** to **2d** under the same conditions, in accord with steric hindrance between bidentate ligand and Cp* group. The **2a–d**/MMAO systems afford polystyrenes with high stereospecificities of greater than 98.6% over the entire range studied.

Interestingly, all the titanium complexes **2a–d** display higher catalytic activities towards styrene polymerization, and produce higher molecular weight polystyrenes with higher syndiotacticities than their mother complex Cp*TiCl₃ (see Table 2). When Cp*TiCl₃ was replaced by the titanium complexes bearing bidentate ligand at 70 °C, the syndiotacticity, and \bar{M}_w of the polymers increase by 3.2–3.8%, and 7.6–12%, respectively. This fact indicates that the chelating 2-phenylamino-ethanol derivative ligands with the unique steric effect and transannular structure seem to play an

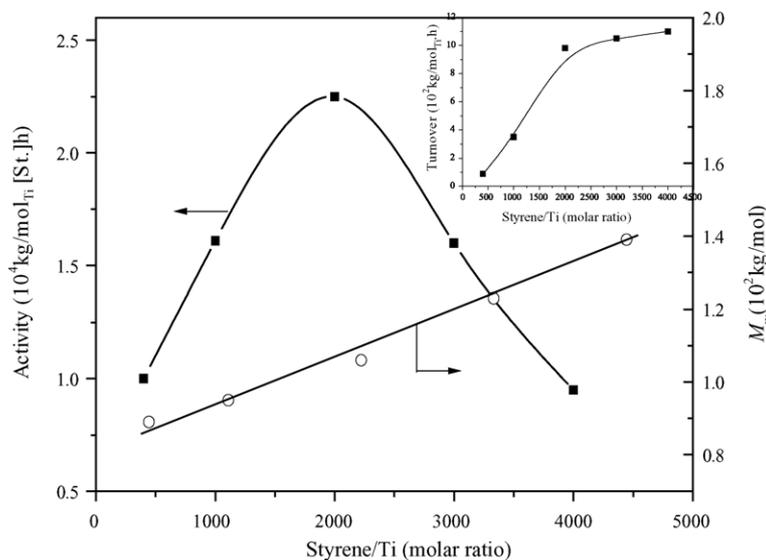


Fig. 3. Plot of activity and \bar{M}_w vs. styrene/Ti molar ratio. A 20 μmol **2a**, Al/Ti = 1000 (molar ratio), $V_{\text{total}} = 100$ mL, polymerization reaction at 70 °C for 10 min.

important role in stabilizing the active species generated from the reaction between the precursors and MMAO. It is known that the type $\text{CpTi}^{\text{III}}\text{R}^+$ for the Cp-based system proposed by Zambelli et al. was accepted as the active species in styrene syndiospecific polymerization [35], although it is still debated in the literature. We tentatively deduce that the lone pair of electrons on the nitrogen atom of 2-phenylamino-ethanol ligand can interact with the Ti^+ (III) species, and then nitrogen atom burdens positive charge which would be delocalized by the p - π conjugation between the nitrogen atom and the aromatic ring. As a result, the active species would become much more stable. The molecular weight distributions for sPS produced by **2a–d**/MMAO show reaction temperature dependence quite different from those by Cp^*TiCl_3 /MMAO due to different structures.

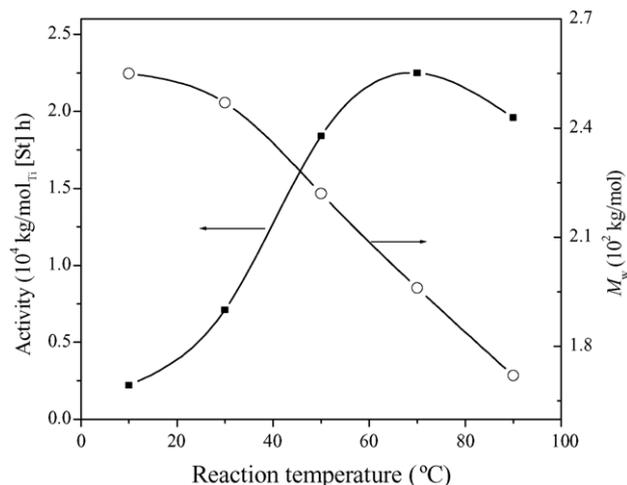


Fig. 4. Plot of activity and \bar{M}_w vs. reaction temperature. 20 μmol **2a**, Al/Ti = 1000 (molar ratio), styrene/Ti = 2200 (molar ratio), $V_{\text{total}} = 100$ mL, polymerization reaction for 10 min.

The complex **3**/MMAO system displays only relatively low catalytic activity towards styrene polymerization at 30 and 50 °C, but its catalytic activity at 70 °C is comparable with that of the Cp^*TiCl_3 /MMAO system. Furthermore, the complex **3**/MMAO system yields higher molecular weight polystyrene with higher syndiotacticities than its mother complex Cp^*TiCl_3 /MMAO system under all the conditions used.

4. Conclusions

In this article, a series of new titanium complexes $\text{Cp}^*\text{TiCl}(\text{OCHRCH}_2\text{NAr})$ ($\text{Cp}^* = \text{C}_5\text{Me}_5$, $\text{R} = \text{H, Me}$; $\text{Ar} = \text{phenyl, 2,6-dimethylphenyl}$) was synthesized and characterized. High catalytic activities can be reached using these complexes activated with MMAO for syndiospecific polymerization of styrene. All the titanium complexes display higher catalytic activity towards the syndiospecific polymerization of styrene in the presence of MMAO as a cocatalyst, yielding higher molecular weight polystyrenes with higher syndiotacticities than their mother complex Cp^*TiCl_3 . Catalytic activities of up to 2.57×10^4 kg sPS/mol $_{\text{Ti}}$ mol $_{\text{St}}$ h, weight-average molecular weights of up to 315 kg/mol, and syndiotacticities of up to 99.1% were observed. Catalytic activities and polymer yields as well as polymer properties are considerably affected by the steric hindrance of bidentate ligands. Catalytic activities, polymer yields, and polymer properties such as syndiotacticity could be controlled in a wide range by changing structure of the catalysts and reaction parameters. A titanium complex $\text{Cp}^*\text{TiCl}_2(\text{OCHMeCH}_2\text{NC}_6\text{H}_3^i\text{Pr}_2\text{-2,6})$ also produces higher molecular weight polystyrenes with higher syndiotacticities, though it shows lower catalytic activity than their mother complex Cp^*TiCl_3 .

5. Supplementary material

Crystallographic data for the structure reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication number CCDC-237699. Copies of the data can be obtained on application to: The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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