

# Steric and electronic effects of the R in $\text{IndTiCl}_2(\text{OR})$ catalysts on the syndiospecific polymerization of styrene

Haiyan Ma, Bin Chen, Jiling Huang, Yanlong Qian\*

*The Laboratory of Organometallic Chemistry, East China University of Science and Technology, Shanghai 200237, PR China*

Received 18 August 2000; accepted 22 January 2001

## Abstract

Four alkoxy ligand substituted indenyl titanium dichloride complexes,  $\text{IndTiCl}_2(\text{OR})$  ( $\text{R} = \text{Me}$  (**2**),  $\text{Et}$  (**3**),  $^i\text{Pr}$  (**4**), cyclohexyl (**5**)) were prepared, and evaluated as catalysts for the syndiospecific polymerization of styrene when activated with methylaluminumoxane (MAO). Alkoxy ligand substituted complexes showed higher catalytic activities than  $\text{IndTiCl}_3$  (**1**) except for complex **5**. When  $\text{R} = \text{Et}$ , the catalyst **3** showed the highest activity. A study of the steric and electronic effects of alkoxy ligand revealed that the more electron-donating and less steric bulky R group was more suitable for the improvement of the catalytic activity. When the polymerization was carried in solution at high molar ratio of  $\text{Al/Ti} = 4000$ , the s-PS% of obtained polymer were in the range of 99.0–99.6%. The highest melting point of 276.9°C was obtained by using **2** as catalyst. The influence of polymerization temperature was also investigated. The maximum polymerization activities were found at 50°C for all of the above complexes, but the percentages of s-PS were insensitive to the polymerization temperature. © 2001 Elsevier Science B.V. All rights reserved.

*Keywords:* Syndiotactic polystyrene; Titanocene; Alkoxy ligand; Steric and electronic effects

## 1. Introduction

Ishihara and co-workers' work [1,2] led to a further search for the new types of s-PS catalysts. In 1993, Ready et al. reported the first s-PS catalyst containing indenyl ligand and found that the  $(\eta^5\text{-indenyl})\text{TiCl}_3/\text{MAO}$  system catalyzed the syndiospecific polymerization of styrene over a wide range of polymerization temperature more effectively than  $\text{CpTiCl}_3/\text{MAO}$  system [3–6]. More efforts were devoted to the syntheses of new kinds of half-sandwich titanocenes and the elucidation of the relationship of precursor structure and its catalytic be-

havior [7–12]. It was found that the electron-donating ability of the  $\pi$ -donor ligands (such as cyclopentadienyl, indenyl, etc.), steric effects and chirality of the ligands attached to the group 4 metal centers strongly influenced the polymerization. The effects of the substituents attached to the cyclopentadienyl or indenyl ligand of  $(\eta^5\text{-Cp})\text{Ti}(\text{O}^i\text{Pr})_3$  and  $(\eta^5\text{-Ind})\text{TiCl}_3$  on the styrene polymerization have been discussed [4–16]. But the effect of the  $\sigma$ -bonded ligands has not been reported properly.

Our previous work proved that one alkoxy ligand substituted complexes of general formula  $\text{CpTiCl}_2(\text{OR})$  were more active than  $\text{CpTiCl}_3$  [17–20]. When  $\text{R} = ^i\text{Pr}$  and cyclohexyl, the catalytic activities were as high as  $6.33\text{--}6.58 \times 10^7 \text{ gPS}/(\text{molTi molS h})$  and were three times as that of  $\text{CpTiCl}_3$  [19]. Were

\* Corresponding author. Fax: +86-21-64702573.  
E-mail address: qianling@online.sh.cn (Y. Qian).

there similar influences on the catalytic activity when a chloride atom was substituted by an alkoxy group in  $\text{IndTiCl}_3$ ?

In this work, we prepared four single-alkoxy-ligand substituted indenyl titanium dichloride complexes of general formula  $\text{IndTiCl}_2(\text{OR})$  ( $\text{R} = \text{Me}$  (**2**),  $\text{Et}$  (**3**),  $^i\text{Pr}$  (**4**), cyclohexyl (**5**)), and compared their catalytic behavior with  $\text{IndTiCl}_3$  in the syndiospecific polymerization of styrene.

## 2. Experimental

### 2.1. General procedures

All operations were carried out under an argon atmosphere using the standard Schlenk techniques. Tetrahydrofuran, toluene, hexane were distilled from sodium/benzophenone ketyl under argon prior to use. Methylene chloride was distilled under argon from phosphoric anhydride. Methanol and ethanol were refluxed with sodium under argon then were distilled. Isopropanol, cyclohexanol were refluxed with  $\text{CaH}_2$  under argon, then were distilled under reduced pressure. Methylaluminoxane (MAO) was produced by Witco GmbH. Styrene was purified by distillation under reduced pressure twice, and stored at  $-20^\circ\text{C}$  in darkness prior to use.

$^1\text{H}$  NMR spectra were recorded on a Varian GERMINI-300 spectrometer. IR spectra were recorded on a Nicolet MAGNA-IR 500 spectrometer. Mass spectra were obtained at 70 eV using a HP 5989A mass spectrometer. Elemental analyses were performed on an EA-1106 spectrometer. X-ray structure was determined by a Rigaku AFC7R diffractometer with graphite monochromatic  $\text{Mo K}\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ) and a 12 W rotating anode generator.

### 2.2. Preparation of $\text{IndTiCl}_3$ (**1**)

$\text{IndTiCl}_3$  was synthesized according to the literature method [3]. Indene was treated with  $n\text{-BuLi}$  to give indene lithium. The indene lithium reacted with  $\text{Me}_3\text{SiCl}$  to obtain 1-SiMe<sub>3</sub>Ind in 73%. 1-SiMe<sub>3</sub>Ind was added dropwise to the solution of  $\text{TiCl}_4$  in  $\text{CH}_2\text{Cl}_2$ , then the solvent was removed to give a dark red solid. After recrystallization, dark red crystals were separated.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7.81 (m, 2H),

7.55 (m, 2H), 7.19 (d, 2H,  $J = 12 \text{ Hz}$ ), 7.16 (t, 1H,  $J = 12 \text{ Hz}$ ).

### 2.3. Preparation of $\text{IndTiCl}_2(\text{OMe})$ (**2**)

The complex was synthesized according to a modified literature method [21]. A solution of  $n\text{-BuLi}$  (3.75 mmol) in 10 ml  $n\text{-hexane}$  was treated with dry methanol (0.1200 g, 3.75 mmol) in 1.7 ml  $n\text{-hexane}$  and 1 ml THF at room temperature. After the end of gas evolution, the mixture was cooled to  $-40^\circ\text{C}$  and treated with a solution of  $\text{IndTiCl}_3$  (1.010 g, 3.75 mmol) in 25 ml  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was slowly warmed to ambient temperature, and stirred overnight. Then it was filtered and concentrated. The obtained solid was recrystallized with  $\text{CH}_2\text{Cl}_2$  and  $n\text{-hexane}$  to afford red crystals in 63.6%.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7.80 (m, 2H), 7.45 (m, 2H), 6.87 (m, 2H), 6.82 (m, 1H), 4.37 (s, 3H).

### 2.4. Preparation of $\text{IndTiCl}_2(\text{OEt})$ (**3**)

A solution of  $n\text{-BuLi}$  (4.34 mmol) in 14 ml  $n\text{-hexane}$  was treated with a solution of dry ethanol (0.200 g, 4.34 mmol) in 2.5 ml  $n\text{-hexane}$  at room temperature. After the end of gas evolution, the mixture was cooled to  $-50^\circ\text{C}$  and treated with a solution of  $\text{IndTiCl}_3$  (1.17 g, 4.34 mmol) in 25 ml  $\text{CH}_2\text{Cl}_2$ . The reaction mixture was slowly warmed to ambient temperature, and stirred overnight. After filtration, the solvent was removed under reduced pressure to give a red solid. The solid was washed with  $n\text{-hexane}$  twice and dried under vacuum. Recrystallization of the solid with  $\text{CH}_2\text{Cl}_2/n\text{-hexane}$  afforded red crystals in 58%, mp  $86\text{--}88^\circ\text{C}$ .  $^1\text{H}$  NMR ( $\delta$ , ppm): 7.79 (dd, 2H,  $J = 6.3 \text{ Hz}$ ,  $J = 3.0 \text{ Hz}$ ), 7.45 (dd, 2H,  $J = 6.3 \text{ Hz}$ ,  $J = 3.0 \text{ Hz}$ ), 6.84 (d, 2H,  $J = 3.4 \text{ Hz}$ ), 6.80 (t, 1H,  $J = 3.4 \text{ Hz}$ ), 4.60 (q, 2H,  $J = 5.3 \text{ Hz}$ ), 1.31 (t, 3H,  $J = 5.3 \text{ Hz}$ ). IR (KBr,  $\text{cm}^{-1}$ ): 3300s, 1620m, 1460w, 1390w, 1050w, 880s, 825s. MS ( $m/e$ ): 277 (5.14, M-H), 243 (4.51, M-Cl), 198 (5.19, M-OEt-Cl), 115 (100, indenyl). Anal. Calcd. for  $\text{C}_{11}\text{H}_{12}\text{Cl}_2\text{OTi}$ : C, 47.36%; H, 4.34%. Found: C, 47.21%; H, 4.29%.

### 2.5. Preparation of $\text{IndTiCl}_2(\text{O}^i\text{Pr})$ (**4**)

The same procedure as that described for  $\text{IndTiCl}_2(\text{OEt})$  was used. Red needle crystals were obtained

in 76%, mp 78–80°C.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7.80 (dd, 2H,  $J = 6.3$  Hz,  $J = 3.1$  Hz), 7.45 (dd, 2H,  $J = 6.3$  Hz,  $J = 3.1$  Hz), 6.82 (d, 2H,  $J = 3.4$  Hz), 6.78 (t, 1H,  $J = 3.4$  Hz), 4.92 (m, 1H,  $J = 6.1$  Hz), 1.38 (d, 6H,  $J = 6.1$  Hz). IR (KBr,  $\text{cm}^{-1}$ ): 3330s, 1613m, 1458w, 1392w, 1360w, 1315w, 1200w, 1168w, 1114w, 1050w, 884s, 768s. MS ( $m/e$ ): 292 (1.98,  $M^+$ ), 257 (3.00, M–Cl), 250 (5.38, M–CH<sub>2</sub>=CH–CH<sub>3</sub>), 233 (6.51, M–O<sup>i</sup>Pr), 198 (2.88, M–O<sup>i</sup>Pr–Cl), 115 (100, indenyl). Anal. Calcd. for C<sub>12</sub>H<sub>14</sub>Cl<sub>2</sub>OTi: C, 49.19%; H, 4.82%. Found: C, 48.81%; H, 4.76%.

### 2.6. Preparation of IndTiCl<sub>2</sub>( $\sigma$ -C<sub>6</sub>H<sub>5</sub>) (5)

Complex **5** was prepared according the method described for IndTiCl<sub>2</sub>(OEt). Orange needle crystals were obtained in 61.3%, mp 88–90°C.  $^1\text{H}$  NMR ( $\delta$ , ppm): 7.78 (dd, 2H,  $J = 6.4$  Hz,  $J = 3.0$  Hz), 7.41 (dd, 2H,  $J = 6.4$  Hz,  $J = 3.0$  Hz), 6.82 (d, 2H,  $J = 3.4$  Hz), 6.79 (t, 1H,  $J = 3.4$  Hz), 4.70 (m, 1H), 2.3–1.0 (m, 10H). IR (KBr,  $\text{cm}^{-1}$ ): 3300s, 2930m, 2865m, 1615m, 1460w, 1398w, 1370w, 1055m, 1020w, 885s, 770s. MS ( $m/e$ ): 332 (0.60,  $M^+$ ), 233 (1.92, M– $\sigma$ -C<sub>6</sub>H<sub>5</sub>), 216 (1.72, M–indenyl), 198 (2.74, M– $\sigma$ -C<sub>6</sub>H<sub>5</sub>–Cl), 115 (100, indenyl), 99 (1.07,  $\sigma$ -C<sub>6</sub>H<sub>5</sub>). Anal. Calcd. for C<sub>15</sub>H<sub>18</sub>Cl<sub>2</sub>OTi: C, 54.09%; H, 5.45%. Found: C, 53.93%; H, 5.35%.

### 2.7. Polymerization and polymer characterization

A small ampoule bottle that was baked under vacuum and filled with argon for several times was used for polymerization, 2 ml (runs in solution) or 11 ml (runs in bulk) of styrene, various proportions of toluene or without toluene, MAO (10 wt.% in toluene) and various proportions of 0.05 mol/l Ti compound in toluene were injected into the bottle in this order under an argon atmosphere. The total volume was 12 ml. The bottle was put into an oil bath for a certain time. The polymerization mixture was quenched with 10% HCl in ethanol, filtered, washed and dried in vacuum oven at 80°C for 24 h to a constant weight. The polymer was then extracted with 2-butanone for 2 h to remove any atactic polymer. The *s*-PS% was determined as the amount of polymer insoluble in 2-butanone. Melting points of the obtained syndiotactic polystyrene were determined by DSC. The

thermograms were recorded with a DSC 2910 Modulated DSC Universal V1.10B TA Instruments.

## 3. Results and discussions

When the indenyl trichloro complex IndTiCl<sub>3</sub> was treated with the lithium salt of the corresponding alcohol, catalysts **2–5** were obtained in moderate yield as dark red to orange crystals.

Crystallization of catalyst **5** from CH<sub>2</sub>Cl<sub>2</sub>/*n*-hexane at –20°C afforded crystals suitable for X-ray analysis. The molecular structure, selected bond distances and angles for **5** were given in Fig. 1. It was composed by two separated molecules with different intramolecular dimension slightly.

The crystal structure showed clearly a piano-stool configuration with the indenyl penta-hapto bonded to the tetravalent titanium center with a ring centroid bond distance of 2.059–2.065 Å, which was little longer than the one in IndTiCl<sub>3</sub> [3]. The alkoxy group was coordinated as a pronounced  $\pi$ -donor, as evidenced by the short titanium oxygen length of 1.715(2)–1.718(2) Å and the obtuse angle at the oxygen of 159.0(3). The same interaction of oxygen to titanium was also found in the similar complex **2** [21]. Thus, we thought this kind of interaction in alkoxy substituted complexes might have significant influence on the catalytic behavior.

Table 1 summarized the influence of alkoxy ligands on the polymerization of styrene in solution. Generally, the catalytic activity and the *s*-PS% increased with the increasing of Al/Ti from 2000 to 4000, which was in agreement with those reported by Ishihara [2]. The *s*-PS% at high molar ratio of Al/Ti = 4000 were very high as more than 99%.

As shown in Table 1, the substitution of alkoxy ligands did have some influence on the catalytic activities of the complexes. Alkoxy ligand substituted complexes showed higher catalytic activities than IndTiCl<sub>3</sub> except for complex **5**. Complex **3** showed the highest activity among the five complexes. We thought the substitution of alkoxy ligands introduced some electronic effects compared to IndTiCl<sub>3</sub>. The strong  $\pi$ -donation of oxygen to titanium center decreased both the bonding of titanium indenyl and titanium chlorine, which could be deduced from the longer lengths in complex **5** than in IndTiCl<sub>3</sub> [3]. The weak-

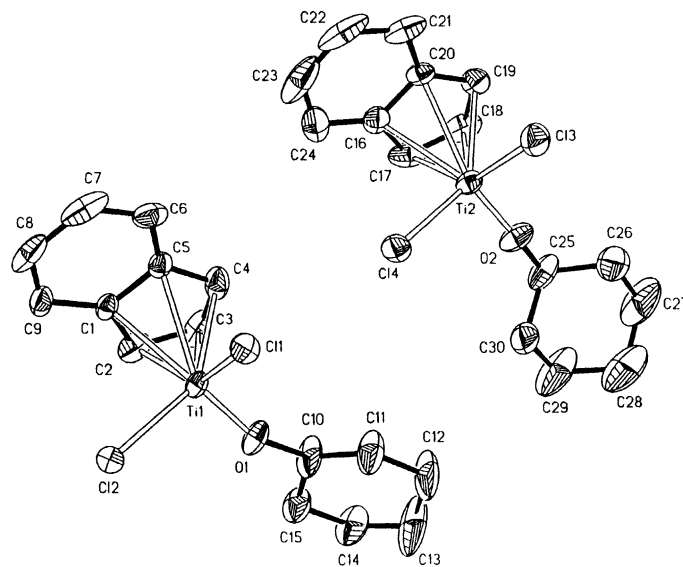


Fig. 1. X-ray structure and selected bond distances (Å) and bond angles (°) for **5**: Ti(1)–O(1) 1.718(2), Ti(1)–Cl(1) 2.2526(10), Ti(1)–Cl(2) 2.2719(10), Ti(1)–C(1) 2.469(3), Ti(1)–C(2) 2.333(3), Ti(1)–C(3) 2.306(3), Ti(1)–C(4) 2.320(4), Ti(1)–C(5) 2.469(3), Ti(1)–C1–C5 2.059, Ti(2)–O(2) 1.715(2), Ti(2)–Cl(3) 2.2657(12), Ti(2)–Cl(4) 2.2575(11), Ti(2)–C(16)–C(20) 2.065; Cl(1)–Ti(1)–Cl(2) 103.97(4), O(1)–Ti(1)–Cl(1) 103.30(9), O(1)–Ti(1)–C(2) 107.10(12), O(1)–Ti(1)–C(3) 88.35(12), O(1)–Ti(1)–C(4) 104.45(12), O(1)–C(10)–C(11) 112.9(3), C(15)–C(10)–O(1) 115.2(3), C(10)–O(1)–Ti(1) 159.0(3), Cl(3)–Ti(2)–Cl(4) 102.85(4).

ening of Ti–Cl bonding might make easier the methylation and ligands abstraction that were thought to lead to the formation of the active species [22]. From this point of view, the introducing of the alkoxy ligand might increase the formation rate of the active species

and also the concentration of it, thus, might lead to the increase of the catalytic activity. Since the complex **5** still showed lower activity than IndTiCl<sub>3</sub>, we thought the substitution of alkoxy ligand also introduced some steric effects. The alkoxy ligand that was

Table 1  
Syndiospecific polymerization of styrene in solution catalyzed by **1–5** and MAO<sup>a</sup>


Run no.	Catalyst	[Ti] (mM)	Al/Ti (10 <sup>3</sup> )	Time (h)	Yields PS (g)	Conversion (%)	A <sup>b</sup> (10 <sup>6</sup> )	s-PS <sup>c</sup> (%)	T <sub>m</sub> (°C)
1	IndTiCl <sub>3</sub> ( <b>1</b> )	0.42	2.0	1	0.1450	8.0	1.67	95.9	–
2		0.21	4.0	1	0.1500	8.3	3.45	98.9	275.0
3	IndTiCl <sub>2</sub> (OMe) ( <b>2</b> )	0.42	2.0	1	0.1955	10.8	2.25	95.8	–
4		0.21	4.0	1	0.1616	8.9	3.72	99.3	276.9
5	IndTiCl <sub>2</sub> (OEt) ( <b>3</b> )	0.42	2.0	1	0.2970	16.4	3.41	97.7	–
6		0.21	4.0	1	0.2109	11.6	4.85	99.6	274.7
7	IndTiCl <sub>2</sub> (O <sup>i</sup> Pr) ( <b>4</b> )	0.42	2.0	1	0.1823	10.1	2.10	98.2	–
8		0.21	4.0	1	0.1736	9.6	3.99	99.1	273.3
9	IndTiCl <sub>2</sub> (O-C <sub>6</sub> H <sub>11</sub> ) ( <b>5</b> )	0.42	2.0	1	0.1221	6.7	1.40	97.2	–
10		0.21	4.0	1	0.1250	6.9	2.87	99.0	273.9

<sup>a</sup> Polymerization conditions: 2 ml styrene; [Al] = 0.83 M; [S] = 1.45 M; T<sub>p</sub> = 50°C.

<sup>b</sup> gPS/(molTi molS h).

<sup>c</sup> g of 2-butanone insoluble polymer/g of bulk polymer.

Table 2  
Syndiospecific polymerization of styrene in bulk catalyzed by 1–5 and MAO<sup>a</sup>

Run no.	Catalyst	[Ti] (mM)	Al/Ti	Temperature (°C)	Time (h)	Yields PS (g)	Conversion (%)	A <sup>b</sup> (10 <sup>6</sup> )	s-PS <sup>c</sup> (%)
11	IndTiCl <sub>3</sub> (1)	0.42	300	50	0.5	1.0117	10.2	4.23	83.7
12		0.21	300	50	0.5	1.0996	11.0	9.19	86.4
13	IndTiCl <sub>2</sub> (OMe) (2)	0.42	300	50	0.5	1.3244	13.3	5.54	87.8
14		0.21	300	50	0.5	1.5709	15.8	13.1	90.1
15	IndTiCl <sub>2</sub> (OEt) (3)	0.42	300	50	0.5	1.5117	15.2	6.32	88.4
16		0.21	300	50	0.5	1.6676	16.7	13.9	90.1
17	IndTiCl <sub>2</sub> (O <sup>i</sup> Pr) (4)	0.42	300	50	0.5	0.9711	9.8	4.06	85.2
18		0.21	300	50	0.5	0.6765	6.8	5.66	81.3
19	IndTiCl <sub>2</sub> (O-  ) (5)	0.42	300	50	0.5	0.7794	7.8	3.26	79.2
20		0.21	300	50	0.5	0.2772	2.3	2.32	61.5

<sup>a</sup> Polymerization conditions: 11 ml styrene; [S] = 7.98 M.

<sup>b</sup> gPS/(molTi molS h).


<sup>c</sup> g of 2-butanone insoluble polymer/g of bulk polymer.

considered to have been stripped during the formation of the active species might still surround the active species. When R was cyclohexyl, a bulky group, the coordination and insertion of styrene to the titanium center might be hindered due to the surrounding of

the bulk alkoxy group, reflected in the decrease of the activity.

Certainly, the substitutions of the other three alkoxy ligands also introduced some steric effects. Compared to the electron-donating ability, the steric effects were

Table 3  
The effect of polymerization temperature<sup>a</sup>

Catalyst	[Ti] (mM)	Al/Ti	Temperature (°C)	Time (h)	Yields PS (g)	Conversion (%)	A <sup>b</sup> (10 <sup>6</sup> )	s-PS <sup>c</sup> (%)
IndTiCl <sub>3</sub> (1)	0.42	300	25	0.5	0.5242	5.3	2.19	65.1
	0.42	300	50	0.5	1.0117	10.2	4.23	83.7
	0.42	300	70	1	1.4586	14.6	3.05	86.6
	0.42	300	90	2	1.5403	15.5	1.61	80.0
IndTiCl <sub>2</sub> (OMe) (2)	0.42	300	25	0.5	0.9766	9.8	4.08	85.2
	0.42	300	50	0.5	1.3244	13.3	5.54	87.8
	0.42	300	70	1	1.6544	16.6	3.46	90.3
	0.42	300	90	2	1.8724	18.8	1.95	87.7
IndTiCl <sub>2</sub> (OEt) (3)	0.42	300	25	0.5	0.9050	9.1	3.78	83.3
	0.42	300	50	0.5	1.5117	15.2	6.32	88.4
	0.42	300	70	1	1.7451	17.5	3.65	91.2
	0.42	300	90	2	2.2418	22.5	2.34	90.7
IndTiCl <sub>2</sub> (O <sup>i</sup> Pr) (4)	0.42	300	25	0.5	0.6550	6.6	2.74	77.7
	0.42	300	50	0.5	0.9711	9.8	4.06	85.2
	0.42	300	70	1	0.9550	9.6	2.00	80.3
	0.42	300	90	2	1.5126	15.2	1.58	81.9
IndTiCl <sub>2</sub> (O-  ) (5)	0.42	300	25	0.5	0.5462	5.5	2.28	70.5
	0.42	300	50	0.5	0.7794	7.8	3.26	79.2
	0.42	300	70	1	0.9459	9.5	1.98	79.2
	0.42	300	90	2	1.3250	13.3	1.38	77.1

<sup>a</sup> Polymerization conditions: 11 ml styrene; [Al]=0.125M; [S]=7.98 M.

<sup>b</sup> gPS/(molTi.molS.h).

<sup>c</sup> g of 2-butanone insoluble polymer/g of bulk polymer.

rather weak, thus, complexes **2** and **3** showed higher catalytic activities than  $\text{IndTiCl}_3$ , and complex **3** showed highest activity. When R was isopropyl, there existed the steric and electronic effects either of them would be the dominant factor due to the different polymerization conditions. Under the given conditions in Table 1, the electronic effect became the dominant factor, thus, the activity increased.

When we carried the polymerization in bulk with a low molar ratio of  $\text{Al/Ti} = 300$  (Table 2), the steric hindrance became a further dominant factor due to the high monomer concentration, as a result, complexes **4** and **5** showed lower catalytic activities than  $\text{IndTiCl}_3$ . Complex **3** still showed the highest activity (run 15, 16).

The percentages of syndiotactic polystyrene were not as high as those in Table 1. High styrene concentration increased both the syndiospecific polymerization rate and the aspecific polymerization rate [23,24].

The catalytic activities were higher than those in Table 1 ( $\text{Al/Ti} = 2000\text{--}4000$ ). As shown in Table 2, the activities of complexes **1**, **2** and **3** increased twice with the decrease of  $[\text{Ti}]$  from 0.42 to 0.21 mmol/l at a constant  $\text{Al/Ti}$  (run 11 with 12 and so on). It was suggested that the polymerization rates were almost same for  $[\text{Ti}] = 0.21\text{--}0.42$  mmol/l due to the very high styrene concentration. As to complexes **4** and **5**, because of the steric hindrance, the activities did not increase so much as those of complexes **1**, **2** and **3** (run 17, 18 and so on).

We also investigated the influence of temperature on the syndiospecific polymerization of styrene in bulk.

From the results in Table 3, we found the maximum polymerization activities were obtained at  $50^\circ\text{C}$ . Higher temperature ( $90^\circ\text{C}$ ) led to the decrease of the activities. The percentages of s-PS obtained by alkoxy ligand substituted complexes were affected slightly by the polymerization temperature. Furthermore, unlike the cyclopentadienyl analogues [19,20], the indenyl complexes **2–5** exhibited high syndiospecificities even at low polymerization temperature of  $25^\circ\text{C}$ .

#### 4. Conclusions

The results of this study indicated that alkoxy ligand substituted complexes showed higher catalytic activities than  $\text{IndTiCl}_3$  (**1**) except for complex **5**, and the

more electron-donating and less steric bulky R group was more suitable for the improvement of the catalytic activity. When the polymerization was carried in solution at high molar ratio of  $\text{Al/Ti} = 2000\text{--}4000$ , the s-PS% of obtained polymer were in the range of 95.8–99.6%. The highest melting point of  $276.9^\circ\text{C}$  was obtained by using **2** as catalyst. The maximum polymerization activities were found at  $50^\circ\text{C}$  for all of the complexes. The percentages of s-PS obtained by the alkoxy ligand substituted complexes were insensitive to the polymerization temperature.

#### Acknowledgements

We gratefully acknowledge the financial support from the Special Funds for Major State Basic Research Projects (G1999064801), National Natural Science Foundation of China (NNSFC) and Sino Petroleum Company (29734145), and NNSFC (29871010).

#### References

- [1] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2464–2465.
- [2] N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356–3360.
- [3] T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, *Macromolecules* 26 (1993) 5822–5823.
- [4] P. Foster, T.E. Ready, J.C.W. Chien, M.D. Rausch, *Polym. Prep.* 37 (1) (1996) 258–259.
- [5] P. Foster, J.C.W. Chien, M.D. Rausch, *Organometallics* 15 (1996) 2404–2409.
- [6] T.E. Ready, J.C.W. Chien, M.D. Rausch, *J. Organomet. Chem.* 519 (1996) 21–28.
- [7] G. Xu, E. Ruckenstein, *J. Polym. Sci. A: Polym. Chem.* 37 (1999) 2481–2488.
- [8] N. Schneider, M.-H. Prosenc, H.-H. Brintzinger, *J. Organomet. Chem.* 545/546 (1997) 291–295.
- [9] M.S. Blais, J.C.W. Chien, M.D. Rausch, *Organometallics* 17 (1998) 3775–3783.
- [10] G. Tian, S. Xu, Y. Zhang, B. Wang, X. Zhou, *J. Organomet. Chem.* 558 (1998) 231–233.
- [11] R. Duchateau, H.C.L. Abbenhuis, R.A. Santen, S.K.-H. Thiele, M.F.H. Tol, *Organometallics* 17 (1998) 5222–5224.
- [12] J.C. Flores, T.E. Ready, J.C.W. Chien, M.D. Rausch, *J. Organomet. Chem.* 562 (1998) 11–15.
- [13] W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, *Macromolecules* 30 (1997) 7647–7650.
- [14] W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3907–3945.

- [15] Q. Wu, Z. Ye, S. Lin, *Macromol. Chem. Phys.* 198 (1997) 1823–1828.
- [16] Y. Kim, B.H. Koo, Y. Do, *J. Organomet. Chem.* 527 (1997) 155–161.
- [17] J. Liu, J. Huang, Y. Qian, *Polym. Bull.* 37 (1996) 719–721.
- [18] J. Liu, J. Huang, Y. Qian, F. Wang, A.S.C. Chan, *Polym. J.* 29 (2) (1997) 182–183.
- [19] J. Liu, H. Ma, J. Huang, Y. Qian, *Eur. Polym. J.* 36 (2000) 5055–5058.
- [20] H. Ma, Y. Zhang, B. Chen, J. Huang, Y. Qian, *J. Polym. Sci. A: Polym. Chem.*, 2000, unpublished results.
- [21] J. Okuda, P. König, I.L. Rushkin, H.-C. Kang, W. Massa, *J. Organomet. Chem.* 501 (1995) 37–39.
- [22] R. Pó, N. Cardi, *Prog. Polym. Sci.* 21 (1996) 47–88.
- [23] J.C.W. Chien, Z. Salajka, *J. Polym. Sci. Polym. Chem.* 29 (1991) 1243–1251.
- [24] J.C.W. Chien, Z. Salajka, *J. Polym. Sci. Polym. Chem.* 29 (1991) 1253–1263.