(ArO)TiR₃ complexes for highly syndiospecific styrene polymerizationChongjie Xu^a, Zhou Chen^b, Gang Ji^b, Xiu-Li Sun^{b,*}, Jun-Fang Li^b, Yong Tang^b^a School of Chemistry and Chemical Engineering, Suzhou University, Suzhou 215123, China^b State Key Laboratory of Organometallic Chemistry, Shanghai Institute of Organic Chemistry, 345 Lingling Lu, Shanghai 200032, China

ARTICLE INFO

Article history:

Received 31 July 2013

Received in revised form

24 November 2013

Accepted 28 November 2013

Available online 6 December 2013

Keywords:

Phenolate

Titanium(IV) complexes

High temperature

Polystyrene

Syndiotactic

ABSTRACT

A kind of (ArO)TiR₃ (ArO = 2,6-(R')₂-4-methylphenolate, R' = Me, ^tBu, CH₂SPh, CH₂N(ⁱPr)₂, CH₂NPh₂) complexes was synthesized and characterized. X-ray analysis of **6a** and **7** shows that neither —CH₂SPh (**6a**) nor —CH₂N(ⁱPr)₂ group (**7**) coordinates to titanium. Large bond angles C(Ar)-O(1)-Ti(1) angle (152.9(2)° in **6a** and 175.33° in **7**) indicate that the bond have partial sp²-hybridized character. Upon treatment with modified methylaluminoxane (MMAO), the titanium complexes exhibit significant thermal stability, and prove useful as styrene syndiotactic polymerization catalysts. Comparisons between different complexes on the styrene polymerization were discussed. Steric instead of electronic properties at 2,6-positions of phenol affect the polymerization activity. (2-tert-Butyl)-4-methylphenoxytitanium(IV) chloride **5e** was established the most efficient one. High activity (1.11 × 10⁵ g sPS/mol(Ti)h) was achieved when styrene polymerization was carried out in the presence of **5e**/MMAO at 130 °C for 2 h.

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1. Introduction

Syndiotactic polystyrene (sPS) is a kind of important engineering plastic because of its high crystallinity, high modulus of elasticity, low dielectric constant, and excellent resistance to heat and chemicals [1]. CpTiCl₃ and its derivatives have been proved to be excellent catalyst since their discovery in the mid 1980s [2]. Moreover, tremendous efforts [3–10] have been made to develop new catalytic systems. Of them, chelate ligands or η⁵-cyclopentadienyl derivatives were usually designed to modulate the properties of active species. For example, Okuda disclosed that bis(phenolato)titanium complexes ((OC₆H₂-4-Me-6-^tBu)₂)TiX₂, X = Cl, OⁱPr, C₅Me₅) were highly active to polymerize styrene syndiospecifically [6a]. FI catalyst based on phenoxy-imine/MMAO was reported to form highly syndiotactic polystyrene [6d]. In addition, rare metal complexes were also documented for this polymerization. For example, (Z5-2,5-^t-Bu₂C₄H₂N)Sc(CH₂C₆H₄NMe₂-O)₂/[Ph₃C][B(C₆F₅)₄] developed by Hou and coworkers afforded high molecular weight syndiotactic polystyrene in high activity [9c]. Mono(indenyl)-Sc-dialkyl/[Ph₃C][B(C₆F₅)₄] developed by Chen et al. was extremely efficient in producing syndiopolystyrene [9f]. Recently, a monomeric pentamethylcyclopentadienyltitananes bearing more than two pairs of methyl substituents on the side arms of triethanolamines was reported to catalyze the styrene polymerization at 110 °C for 10 min in an activity of 31.7 g

of PS/(mol(Ti)molstyrene h). The steric bulkiness in tetradentate ligands has great influence on the polymerization and the activity drastically decreased in the case of Cp*Ti(OCH₂CH₂)₃N (Cp* = pentamethylcyclopentadienyl) being used [8b].

Phenol derivatives were usually used as anionic ancillary ligands to replace Cl⁻ in half titanocenes, and the cooperative effect of Cp and phenolate was believed to affect the syndiospecific styrene polymerization activity [11]. So far, cationic [Cp'Ti(polymer)(styrene)]⁺ (Cp' = cyclopentadienyl and its derivatives) was assumed to play an essential role for the styrene polymerization. We [12] recently found that simple phenolate titanium(IV) complexes ArOTiX₃ (X = NMe₂, Cl, CH₂Ph) could promote the styrene syndiotactic polymerization smoothly at above 100 °C, and the properties of phenolate have distinctive influence on the catalytic activity. In the presence of MMAO, the complexes exhibit good activity and excellent thermostability for the syndiotactic polymerization of styrene. Steric instead of electronic properties at 2,6-positions of phenol affect the polymerization activity. (2-tert-Butyl)-4-methyl-phenoxytitanium(IV) trichlorides **5e** was established the most efficient one. sPS was obtained in an activity of 1.11 × 10⁵ g sPS/mol(Ti) h even when the polymerization proceeded at 130 °C for 2 h. We report the results in detail.

2. Experimental

2.1. Materials

All manipulations were carried out under argon or nitrogen atmosphere using standard Schlenk or glove box techniques.

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Toluene, THF, hexane and dichloromethane were treated with solvent purification MB SPS-800 prior to use. Styrene was dried over CaH₂ under stirring for 48 h and distilled before use. The purified styrene was stored in the refrigerator under nitrogen and used within a week. Modified methylaluminoxane (MMAO-3A) was purchased from Akzo Chemical as 1.88 M heptane solution.

Molecular weight (M_w and M_n) and molecular weight distribution (M_w/M_n) of sPS were determined with a PL-220 GPC at 150 °C (using polystyrene calibration, 1,2,4-trichlorobenzene as the solvent at a flow rate of 1.0 mL/min). ¹H NMR and ¹³C NMR spectra were recorded on a Varian XL-300 MHz and Varian XL-400 MHz spectrometer. Mass spectra were obtained using a HP5959A spectrometer. Elemental analysis was performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). ¹³C NMR data for polymers were obtained using CDCl₃ as the solvent at 25 °C. X-ray crystallographic data were collected using a SMART APEXII X-ray diffractometer. Compounds **4d–e** were purchased from ACROS, and **4f** was purchased from TCI. Compounds **2**, **[13] 3**, **[13]** and **5c–e [14a]** were prepared according to literature.

2.2. Synthesis of ligands and complexes

2,6-Bis(Phenylthiomethyl)-4-methylphenol (**4a**). Compound **3** (2.03 g, 10 mmol) in THF (30 mL) was added dropwise to a solution of benzenethiol (2.10 mL, 20 mmol) and triethylamine (2.80 mL, 20 mmol) in THF (30 mL). After stirring for about 10 h, the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to give the product as a pale-yellow oil (2.8 g, 80%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 7.35–7.19 (m, 10H), 6.79 (s, 2H), 6.45 (s, 1H), 4.14 (s, 4H), 2.11 (s, 3H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 150.4, 134.9, 130.1, 129.7, 129.1, 128.4, 126.2, 123.1, 34.3, 19.9. HRMS (EI): calcd for C₂₁H₂₀OS₂ (M⁺) 352.0956; found 352.0956.

2,6-Bis((Diphenylamino)methyl)-4-methylphenol (**4b**). Compound **3** (5.13 g, 25 mmol) in methanol (60 mL) was added dropwise to a solution of diphenylamine (8.46 g, 50 mmol) and triethylamine (7.00 mL, 50 mmol) in methanol (30 mL). After stirring 24 h at room temperature, the precipitated product was filtered and washed with methanol. White solid was obtained by recrystallization from ethyl acetate/petroleum (1/10, v/v). Yield: 7.40 g (63%) ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 8.90 (s, 1H), 7.27–7.22 (m, 8H), 7.09–7.07 (m, 8H), 7.02–6.97 (m, 4H), 6.87 (s, 2H), 4.87 (s, 4H), 2.13 (s, 3H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 151.7, 148.6, 129.2, 128.7, 127.4, 123.4, 122.5, 121.8, 54.5, 20.8. IR (KBr, cm⁻¹): 3036, 2930, 2064, 2496, 1589, 1490, 1448, 1366, 1246, 1223, 1195, 1153, 1098, 1085, 1074, 1034, 993, 865, 763, 746, 725, 698. MS (EI): m/z = 470 (M⁺), 169 (Ph₂N). HRMS (EI): calcd for C₃₃H₃₀N₂O (M⁺) 470.2358; found 470.2358.

2,6-Bis((Diisopropylamino)methyl)-4-methylphenol (**4c**). Compound **3** (2.03 g, 10 mmol) in THF (30 mL) was added dropwise to a solution of diisopropylamine (7.00 mL, 50 mmol) and triethylamine (4.20 mL, 30 mmol) in THF (30 mL). The solution was refluxed for 10 h and then cooled to room temperature. The triethylammonium salts were filtered and the solvent was removed under vacuum. The residue was purified by column chromatography on silica gel to give the product as a pale-yellow solid. Yield: 2.8 g (84%). ¹H NMR (300 MHz, CDCl₃): δ (ppm) = 6.96 (s, 2H), 3.71 (s, 4H), 3.09 (m, *J* = 6.6 Hz, 4H), 2.25 (s, 3H), 1.08–1.06 (d, *J* = 6.0 Hz, 24H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 153.5, 127.1, 126.8, 125.0, 47.8, 45.1, 20.7, 20.1. IR (cm⁻¹): 2958, 2933, 2872, 2810, 1612, 1467, 1383, 1296, 1258, 1225, 1187, 1161, 1078, 1028, 985, 864, 840, 787, 747. MS (EI): m/z = 334 (M⁺). HRMS (EI): calcd for C₂₁H₃₈N₂O (M⁺) 334.2984; found 334.2984.

[2,6-Bis(phenylthiomethyl)-4-methylphenolate]Ti(IV)Cl₃(THF) (**5a**). To a stirred solution of **4a** (1.16 g, 3.3 mmol) in toluene (10 mL) was added n-BuLi solution (1.32 mL,

2.5 M in hexane, 3.3 mmol) over a 5 min period at –78 °C. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise within 15 min to TiCl₄(THF)₂ (1.08 g, 3.3 mmol) in toluene (20 mL) at –78 °C with stirring. The mixture was warmed to room temperature and stirred overnight. The dark-red solution was filtered, concentrated and cooled to –30 °C to give dark-red solid. Yield: 1.4 g (72%). ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.40–7.38 (m, 4H), 7.27–7.23 (m, 6H), 6.96 (s, 2H), 4.47 (brs, 4H), 4.44 (s, 4H), 2.24 (s, 3H), 1.97 (brs, 4H). ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 134.6, 133.9, 130.6, 130.1, 129.8, 128.9, 127.9, 125.9, 76.3, 36.4, 25.5, 20.9. Anal. Calcd for C₂₅H₂₆Cl₃O₂Ti (576.83): C 52.05, H 4.54; Found: C 51.77, H 4.62.

[2,6-Bis((diisopropylamino)methyl)-4-methylphenolate]Ti(IV)Cl₃(THF) (**5b**). A same procedure as that for the preparation of **5a** was used. Yield dark-red solid, 2.90 g (61%). ¹H NMR (300 MHz, CDCl₃): δ 7.29 (s, 2H), 4.38 (s, 4H), 4.10 (s, 4H), 3.09 (pent, *J* = 6.5 Hz, 4H), 2.36 (s, 3H), 2.08 (m, 4H), 1.05 (d, *J* = 6.3 Hz, 24H). ¹³C NMR (75 MHz, CDCl₃): ¹³C NMR (100 MHz, CDCl₃): δ (ppm) = 162.9, 128.0, 126.4, 124.9, 76.3, 49.9, 45.2, 26.8, 22.1, 21.4. Anal. Calcd for C₂₅H₄₄Cl₃N₂O₂Ti (558.86): C 53.73, H 7.94, N 5.01; Found: C 52.98, H 8.18, N 4.73.

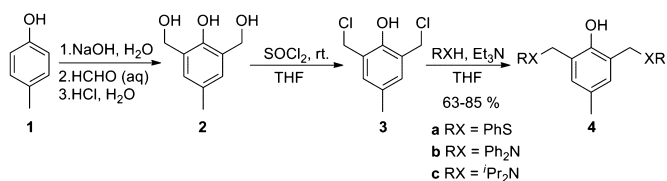
[2-tert-Butyl-4-methylphenolate]Ti(IV)Cl₃(THF) (**5e**). To a solution of TiCl₄ (0.52 mL, 4.7 mmol) in toluene (20 mL) at –78 °C was added dropwise a solution of **4f** (0.77 g, 4.7 mmol) in toluene/THF (8 mL/1 mL) over 10 min, and the resulting mixture was allowed to warm to 65 °C and stirred for 8 h. After removing the solvent under reduced pressure, the brown-red solid was collected and dried in vacuo to give dark-red solid. Yield: 0.74 g (97%) ¹H NMR (400 MHz, CDCl₃): δ (ppm) = 7.60 (d, *J* = 8.0 Hz, 1H), 7.10–7.04 (m, 2H), 4.54 (t, *J* = 6.8 Hz, 4H), 2.37 (s, 3H), 2.12 (pent, *J* = 2.8 Hz, 4H), 1.53 (s, 9H). ¹³C NMR (75 MHz, CDCl₃): δ (ppm) = 168.7, 137.6, 136.3, 128.2, 127.1, 126.6, 76.0, 35.0, 30.4, 25.7, 21.4. Anal. Calcd for C₁₅H₂₃Cl₃O₂Ti (389.57): C 46.25, H 5.95; Found: C 45.86, H 6.30.

[2,6-Bis(phenylthiomethyl)-4-methylphenolate]Ti(IV)(NMe₂)₃ (**6a**). To a solution of Ti(NMe₂)₄ (0.32 g, 1.42 mmol) in toluene (5 mL) at –78 °C was added dropwise a solution of **4a** (0.50 g, 1.42 mmol) in toluene (8 mL) over 5 min, and the resulting mixture was allowed to warm up to room temperature and stirred for 3 h. After removing the solvent under reduced pressure, red solid was obtained and recrystallized in hexane at –30 °C to give red crystal. Yield: 0.70 g (93%). ¹H NMR (400 MHz, C₆D₆): δ (ppm) = 7.32–7.30 (m, 4H), 7.04–6.92 (m, 8H), 4.24 (s, 4H), 3.12 (s, 18H), 2.04 (s, 3H). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) = 159.2, 138.7, 130.6, 129.3, 129.1, 128.9, 125.8, 125.4, 44.6, 34.3, 20.6. Anal. Calcd for C₂₇H₃₇N₃OS₂Ti (531.19): C 61.00, H 7.02, N 7.90; Found: C 60.78, H 7.02, N 7.54.

2,6-Bis((diphenylamino)methyl)-4-methylphenolate Ti(IV)(NMe₂)₃ (**6b**). The same procedure as that for the preparation of **6a** was used. Yellow crystal 0.49 g (yield: 76%). ¹H NMR (300 MHz, C₆D₆): δ (ppm) = 7.39 (s, 2H), 7.28–7.08 (m, 17H), 6.85–6.82 (m, 3H), 5.26 (s, 4H), 3.00 (s, 18H), 1.99 (s, 3H). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) = 158.0, 148.9, 129.6, 129.1, 126.6, 126.4, 121.6, 120.9, 53.2, 44.5, 21.4. Anal. Calcd for C₃₉H₄₇N₅O₂Ti (649.69): C 72.10, H 7.29, N 10.78; Found: C 72.16, H 7.56, N 10.59.

[2,6-di-tert-Butyl-4-methylphenolate]Ti(IV)(NMe₂)₃ (**6c**). The same procedure as that for the preparation of **6a** was used. Yield yellow crystal, 0.37 g (92.6%). ¹H NMR (400 MHz, C₆D₆): δ (ppm) = 7.21 (s, 2H), 3.08 (s, 18H), 2.31 (s, 3H), 1.57 (s, 18H). ¹³C NMR (100 MHz, C₆D₆): δ (ppm) = 162.3, 139.6, 127.7, 125.9, 45.4, 35.2, 30.5, 21.5. Anal. Calcd for C₂₁H₄₁N₃OTi (399.44): C 63.15, H 10.35, N 10.52; Found: C 62.60, H 10.10, N 9.87.

[2,6-Bis((diisopropylamino)methyl)-4-methylphenolate]Ti(IV)Bn₃ (**7**). To a solution of TiBn₄ (0.43 g, 1.0 mmol) in toluene (10 mL) at –78 °C was added dropwise a solution of **4c** (0.32 g, 1.0 mmol) in toluene (10 mL) over 10 min. The resulting mixture was allowed to warm to room temperature and stirred for 3 h. The



Scheme 1. Synthesis of ligands **4**.

dark-red solution was concentrated. The precipitated dark-red solid was filtered and recrystallized from hexane/toluene (30/1) at -30°C . Yield 0.46 g (71%). $^1\text{H NMR}$ (300 MHz, C_6D_6): δ (ppm) = 7.81 (s, 2H), 7.20–7.14 (m, 6H), 7.02–6.90 (m, 9H), 4.08 (s, 4H), 3.14 (pent, $J=6.3$ Hz, 4H), 2.74 (s, 6H), 2.51 (s, 3H), 1.10 (d, $J=6.3$ Hz, 24H). $^{13}\text{C NMR}$ (100 MHz, C_6D_6): δ (ppm) = 163.28, 142.20, 132.58, 131.73, 129.71, 129.33, 126.73, 124.85, 87.66, 49.05, 45.16, 21.92, 21.17. Anal. Calcd for $\text{C}_{42}\text{H}_{58}\text{N}_2\text{OTi}$ (654.790): C 77.04, H 8.93, N 4.28; Found: C 76.73, H 8.53, N 4.16.

2.3. General procedure of styrene polymerization

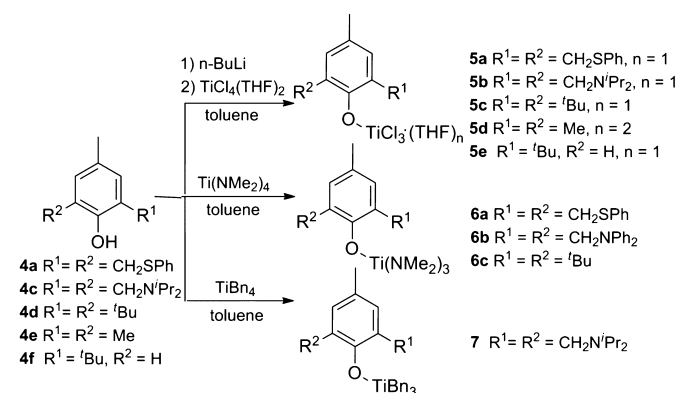
Mixture of desired amount of MMAO and catalyst in toluene (1.88 M, 1 mL) was stirred at room temperature for 15 min. Then styrene was added and the resulting mixture was vigorously stirred at desired temperature. After a desired time, the polymerization was quenched by the fast introduction of acidified ethanol (200 mL, 10% HCl), and the resulting mixture was stirred for 12 h. The polymer was filtered off, washed several times with ethanol, and dried under vacuum until constant weight. sPS and aPS were separated by extracting the polymer with 2-butanone for 12 h.

3. Results and discussion

3.1. Synthesis of ligands and complexes

Compound **2** was accessible from *p*-cresol and aqueous formaldehyde (37.0–40.0%) [13]. After treatment with SOCl_2 , **2** was readily transformed into **3**, which could be used without further purification. In the presence of Et_3N , the reaction between **3** and amine or benzenethiol generated **4** in 63–85% yield (Scheme 1).

Counter-ion usually has distinctive influence on the properties of complexes [11], and we tried to synthesize complexes **5–7** and investigate their performance in styrene polymerization. Titanium (IV) complexes **5–7** were readily available from the corresponding phenol in good yields (Scheme 2). However, in the cases of 2,6-(bis-aminomethyl)-4-methylphenol being used, a mixture of monophenolate and biphenolate titanium complexes was always obtained. The pure **5b**, **6b**, and **7** were isolated by repeated recrystallization.



Scheme 2. Synthesis of complexes **5–7**.

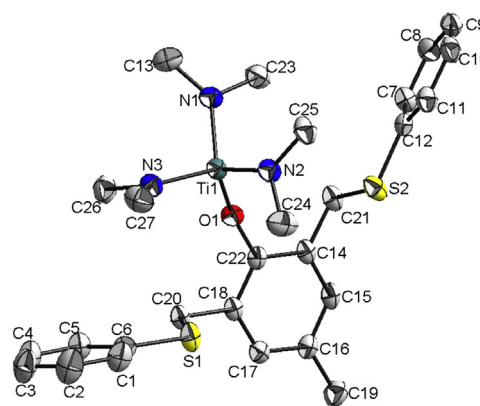


Fig. 1. Molecular structure of complex **6a** (hydrogen atoms were omitted for clarity). Selected bond lengths (Å) and angles (deg): Ti(1)–N(1) = 1.901(3), Ti(1)–N(2) = 1.867(3), Ti(1)–N(3) = 1.892(3), N(2)–Ti(1)–O(1) = 112.20(13), N(2)–Ti(1)–N(3) = 106.48(14), O(1)–Ti(1)–N(3) = 112.86(12), N(2)–Ti(1)–N(1) = 107.87(14), O(1)–Ti(1)–N(1) = 110.51(12), N(3)–Ti(1)–N(1) = 106.61(14), C(18)–C(20)–S(1) = 108.4(2), C(14)–C(21)–S(2) = 108.0(2).

All compounds were well characterized by $^1\text{H NMR}$, $^{13}\text{C NMR}$ and elemental analysis. In the $^1\text{H NMR}$ spectra of the complexes **5a**, **5b**, **6a**, **6b** and **7**, single signal appeared at above 4.00 ppm, which are assigned as the methylene attached to the phenol group and suggested that both amine groups and thioether groups are chemically equal. Fortunately, the structure of complexes **6a** and **7** were further confirmed by X-ray analysis [15] (Figs. 1 and 2). As shown in Fig. 1, complex **6a** adopts a distorted tetrahedral geometry around Ti(IV). Both phenylthioether groups extend outward. The distances between Ti–S(1) and Ti–S(2) are 4.199 Å and 4.274 Å respectively, which are longer than the corresponding sum of van der Waals radius (3.69 Å) [16]. The Ti1–O1 bond length in complex **6a** is longer than that found for **5c** [1.880(2) Å vs 1.750(2) Å] [14a]. Correspondingly, O1–C22 is shortened (1.344(4) Å vs 1.390(2) Å). The angle of C22–O1–Ti1 [152.9(2) $^{\circ}$] indicated that the lone-pair at the oxygen atom back bonding into the unoccupied Ti(3d) or phenyl π system.

The geometry structure of **7** is similar to that of **6a** (Fig. 2, and Table 1). With the substitution of NMe_2 groups by CH_2Ph groups, Ti1–O1 bond length is shortened to 1.7777(17) Å. Bond O1–C22 is lengthened (1.368(3) Å). The coordinative unsaturation around the metal center is compensated by the coordination of the ipso carbon of the benzyl group. For example, Ti–C14–C13 bond angle and Ti–C7–C6 bond angle are 87.69(17) $^{\circ}$ and 105.73(18) $^{\circ}$ respectively, suggesting that the benzyl groups may be involved in η^2 binding interactions with the metal atom. The third benzyl group was

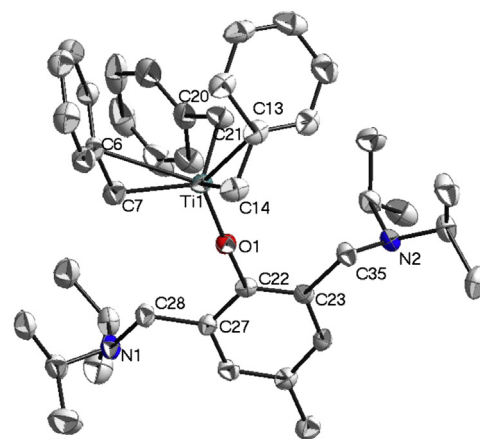


Fig. 2. Molecular structure of complex **7** (hydrogen atoms were omitted for clarity).

Table 1
Selected bond lengths (Å) and angles (deg) of complexes **6a** and **7**.

Entry	6a	7
O(1)–C(22)	1.344(4)	1.368(3)
O(1)–Ti(1)	1.880(2)	1.7777(17)
C(22)–O(1)–Ti(1)	152.9(2)°	175.33(16)
C(6)–C(7)–Ti(1)		105.73(18)
C(13)–C(14)–Ti(1)		87.69(17)
C(20)–C(21)–Ti(1)		114.49(19)

involved in η^1 -bound to the metal (Ti–C21–C20 angle, 114.49(19)°) [17]. The coordination mode of the three benzyl groups in solid state is different from that in solution. $^1\text{H NMR}$ of **7** reveals that only one single signal appears at 2.74 ppm ($-\text{CH}_2\text{Ph}$), which means that the three benzyl groups were chemically equal. $^{13}\text{C NMR}$ of **7** also confirms the speculation since only one single signal at 87.66 ppm appears for three $-\text{CH}_2-$ fragments in benzyl groups. C(22)–O(1)–Ti(1) angle becomes 175.33°, which means that the existence of a d–p π bond between isolated electron pairs at the oxygen atom and the unoccupied Ti(3d) or phenyl π system makes the bond have partial sp-hybridized character. Though we have tried to determine the molecular structure of both **5a** and **5b**, several attempts to develop single crystals failed.

3.2. Styrene polymerization

These titanium complexes proved to be good catalysts for styrene polymerization in the presence of MMAO. Even when the styrene polymerization was carried out at above 100 °C for several hours, moderate to high activities could be achieved with excellent syndiospecificity.

Initially, (mesityloxy)titanium(IV) chloride was tried in styrene polymerization at 110 °C. The products were a mixture of syndiotactic polystyrene (sPS, MEK-insoluble fraction) and atactic polystyrene (MEK-soluble fraction). To our delight, $^{13}\text{C NMR}$ spectroscopy of the MEK insoluble part of the resulting polymer exhibits a single sharp resonance at 145.2 ppm, which is a typical signal for the phenyl ipso carbon atom of the highly syndiotactic polystyrene, and can be attributed to the rrrr structure of the sPS [9a]. The highly syndiotacticity was further confirmed by its melting temperature ($T_m = 268^\circ\text{C}$) [2]. This result indicates a simple phenolate exhibit thermal stability, and could promote the styrene syndiotactic polymerization (Table 2).

Since catalyst would be introduced into the polymerization system as a solution in organic solvent, blank experiments were carried out in 1 mL organic solvent in the presence of MMAO (4000 Al/Ti ratio) at 110 °C. The resulting polymer is soluble in methyl ethyl ketone (MEK), suggesting only atactic polystyrene was generated. Solvent (only 1 mL) affected the results considerably, and the yield

Table 2
Effects of solvents to styrene polymerization with **6b**/MMAO.

Entry ^a	Solvent	Dielectric constant (ϵ)	Styrene polymerization with 6b /MMAO					Blank experiment ^f
			Activity ^b	M_n ^{c,d}	PDI ^d	sPS/PS (%) ^e	aPS ^e (g)	
1	PhCH ₃	2.3	1.33	1.64	2.56	>99	0.04	0.29
2	PhCl	5.7	0.57	0.84	1.87	>99	0.09	0.38
3	PhBr	5.4	0.82	1.12	2.76	>99	0.33	0.51
4	CH ₂ Cl ₂	9.1	–	–	–	–	6.55	4.39
5 ^g	CH ₂ Cl ₂	9.1	–	–	–	–	16.70	

^a Condition: **6b** (10 μmol) in solvent (1 mL), MMAO, Al/Ti = 4000, temperature of bath = 110 °C, $t = 60$ min, $V_{\text{styrene}} = 30$ mL, preaged time = 15 min.

^b 10^5 g sPS/mol(Ti) h.

^c M_n for sPS, 10^4 g/mol.

^d For sPS, determined by GPC.

^e As the amount of aPS was smaller than that produced in the blank experiments, it was concluded that sPS was afforded exclusively.

^f Blank experiment. MMAO, Al/Ti = 4000, temperature of bath = 110 °C, $t = 60$ min, $V_{\text{styrene}} = 30$ mL.

^g **6b** (10 μmol) in CH₂Cl₂ (2 mL).

of atactic polystyrene in the blank experiments increased in the order of PhCH₃ < PhCl < PhBr < CH₂Cl₂ (from 0.29 g to 4.39 g, entries 1–4, Table 2). Considering that replacing 2,6-dimethyl with steric $-\text{CH}_2\text{NPh}_2$ group might benefit the syndiospecificity, **6b** (in 1.0 mL toluene) was first introduced to catalyze the styrene polymerization at 110 °C for 1 h, and an activity of 1.33×10^5 g sPS/mol(Ti) h was achieved (Table 2). Introduction **6b** either in PhCl or in PhBr to the mixture of styrene and MMAO led to the reduction of sPS activity (entry 1 vs 2, 3). The presence of **6b** seems to be able to retard the formation of aPS, since the amount of atactic polystyrene obtained in the presence of **6b** was smaller than that produced in the blank experiments in all cases. On the basis of these results, it was concluded that **6b**/MMAO affords sPS exclusively. Different from the above mentioned, atactic polystyrene was produced solely when **6b** in CH₂Cl₂ was added to styrene polymerization system. Increasing the amount of CH₂Cl₂ led to the improvement of aPS yield. This result is similar to that reported in literature [18]. The yield of aPS increased with a rise in the dielectric constant of the organic solvent, probably because of the different dissociation level of the ion pair [18].

The polymerization conditions strongly influenced activity (Table 3). For example, decreasing the Al/Ti molar ratio from 4000 to 2000 deteriorated the polymerization and halved the activity to 0.62×10^5 g sPS/mol(Ti) h when styrene polymerization was carried out at 110 °C for 1 h. Different from the reported examples [1–10], **6b** showed good stability at high temperatures. For instance, prolonging the polymerization time to 90 min at 110 °C resulted in a slightly increased activity (1.45×10^5 g sPS/mol(Ti) h), and good activity could be reached at elevated temperature as well (entries 3–5). At 130 °C, **6b** can promote the styrene polymerization for at least 60 min to give an activity of 1.09×10^5 g sPS/mol(Ti) h at a Al/Ti ratio of 4000 (entry 5). The deactivation and encapsulation of active species were likely the reason for the activity reduction under this condition. Catalyst aging before styrene polymerization favored the improvement of activities. For example, in the case of **6b** being introduced directly without pretreating with MMAO, the activity was 0.87×10^5 g sPS/mol(Ti) h (entry 3 vs 6). As Ti(III) complexes were generally supposed to be the real catalytic species to catalyze the styrene polymerization, the reason for catalyst aging is probably to reduce Ti(IV) species with MMAO into Ti(III). [19] It is apparent that the initial amount of catalyst not only influence the activity of sPS, but also has an effect on the yield of aPS. 10 μmol **6b** gave the highest activity of sPS. Comparing to 10 or 15 μmol **6b** in the polymerization system, slightly higher amount of aPS was separated when 5 μmol **6b** was used (entry 7 vs 3, 8). This result further elucidated that the presence of **6b** hindered aPS formation.

Either increasing Al/Ti or improving the polymerization temperature led to reduction of M_n of sPS (entries 1–3, 5), suggesting that chain transfer to alkyl aluminum is probably one of the chain

Table 3
Polymerization of styrene with **6b**/MMAO.

Entry ^a	6b (μmol)	Al/Ti	Time (min)	T^b ($^\circ\text{C}$)	Insoluble part				Soluble part	aPS (g) ^g
					Activity ^c	$M_n^{d,e}$	PDI ^e	sPS/PS (%) ^f	aPS (g)	
1	10	2000	60	110	0.62	1.86	2.85	>99	0.03	0.23
2	10	3000	60	110	0.91	1.72	2.67	>99	0.05	0.25
3	10	4000	60	110	1.33	1.64	2.56	>99	0.04	0.29
4	10	4000	90	110	1.45	1.89	2.30	>99	0.11	0.36
5	10	4000	60	130	1.09	0.97	2.37	>99	0.13	0.27
6 ^h	10	4000	60	110	0.87	0.43	4.47	>99	0.11	0.29
7	5	4000	60	110	1.10	1.38	2.51	>99	0.16	0.23
8	15	4000	60	110	0.80	1.37	2.61	>99	0.06	0.31
9 ⁱ	10	4000	60	110	2.60	0.50	1.99	>99		

^a Condition: **6b** in toluene (1 mL), $V_{\text{styrene}} = 30$ mL, aging time = 15 min.^b Temperature of bath, under 1 atm N_2 atmosphere.^c 10^5 g sPS/mol(Ti) h.^d 10^4 g/mol.^e Determined by GPC.^f As the amount of aPS was smaller than that produced in the blank experiments, it was concluded that sPS was afforded exclusively.^g Blank experiment, only MMAO solution and styrene was added.^h **6b** (10 μmol in 1 mL toluene) was added directly without pretreatment with MMAO.ⁱ Catalyst is CpTiCl_3 .

termination way, and high temperature prefers chain transfer to chain propagation. Furthermore, improving Al/Ti as well as the polymerization temperature from 110 to 130 degree narrowed PDI of sPS, suggesting that it takes time to form the catalytic species, and high temperature as well as more MMAO benefit the formation of active species. This guess is also supported by the fact that a wide PDI was achieved when **6b** was used directly without aging. When CpTiCl_3 was used in the presence of 4000 Al/Ti ratio at 110 $^\circ\text{C}$ for 1 h, sPS was formed in 2.60 g sPS/mol(Ti) h.

All complexes were tested active to catalyze the styrene polymerization syndiotactically at 110 $^\circ\text{C}$ and 4000 Al/Ti ratio (Table 4). Of them, complex **5d** bearing mesityloxy group gave the lowest activity (entry 6). Replacing 2,6-dimethyl with 2,6-di-tert-butyl resulted in the activity improvement from 0.96×10^5 g sPS/mol(Ti) h to 1.62×10^5 g sPS/mol(Ti) h (entries 5, 6). The highest activity (1.95×10^5 g sPS/mol(Ti) h) was achieved when 2-(tert-butyl)-4-methyl-phenolate titanium trichloride **5e** was used (entry 7). Complex **5a** derived from

2,6-bis((phenylthio)methyl) group gave a comparable activity with that of **5e** (entry 1 vs 7). Complex **5b** bearing steric 2,6-bis((diisopropylamino)methyl)phenolate showed an even lower activity than that of **5c**. Relative to **5**, both $\text{ArOTi}(\text{NMe}_2)_3$ **6** and ArOTiBn_3 **7** catalyzed the styrene syndiotactic polymerization in lower yields at 110 $^\circ\text{C}$ (entries 10–12). Thus, under the same polymerization conditions, **6c** exhibited lower activity than that of **5c** (entries 5 vs 11). The activity variation probably resulted from the higher BDEs of both Ti–N bond and Ti–C bond than that of Ti–Cl bond [20]. When **5e**, **6b**, or **7** was used without aging, the activities decreased apparently in all cases, whereas **5e** is still the most active one. The complexes were stable over time. However, prolonging the polymerization time led to the catalyst wrap seriously. Consequently, moderate activities were observed when either **5a** or **5e** was used for 4 h at 110 $^\circ\text{C}$ (entries 2 and 8). Even when the polymerization was carried out at 130 $^\circ\text{C}$ for 2 h, 0.80×10^5 g sPS/mol(Ti) h and 1.11×10^5 g sPS/mol(Ti) h were achieved for **5a** and **5e** separately (entries 3 and 9). This is mainly because that the viscous reaction system encapsulated catalyst species and retarded the contact between monomer and the species. In all cases, sPS was afforded exclusively under the conditions, as the amount of aPS was smaller than that produced in the blank experiments even under these conditions. However, $[\text{2,6}-(\text{CH}_2\text{N}^i\text{Pr}_2)_2-4\text{-Me-C}_6\text{H}_3\text{O}]\text{TiBn}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ only produced aPS, probably in a cationic manner [11b].

Mn of the resulting sPS varied around 1×10^4 g/mol except **5d**. **5d** produced sPS with 2.73×10^4 g/mol, probably owing to the small methyl groups on the phenylortho positions. In other cases, little effect of catalyst on molecular weight of the resulting polystyrene was observed. The PDI of the polymers varied in the range of 2.26–3.52 without distinct trend. The reason is unclear.

4. Conclusions

In conclusion, though phenol derivatives were usually used as anionic ancillary ligands to replace Cl^- in half titanocenes, we found that simple phenolate titanium(IV) complexes ArOTiX_3 ($\text{X} = \text{NMe}_2$, Cl , CH_2Ph) could promote the styrene syndiotactic polymerization smoothly at high temperature (110–130 $^\circ\text{C}$) for at least 4 hours. The properties of phenolate have distinctive influence on the catalytic activity. And (2-(tert-butyl)-6-methylphenoxy)titanium(IV) trichlorides gave the highest activity (1.95×10^5 g sPS/mol(Ti) h) in the styrene polymerization at 110 $^\circ\text{C}$. Catalyst aging is beneficial to the polymerization. Since the electronic and steric nature of

Table 4
Influence of catalysts on styrene polymerization.^a

Entry ^a	Cat.	sPS (g) ^b	Activity ^c	$M_n^{d,e}$	PDI ^d
1	5a	0.63	1.89	1.34	3.52
2 ^f	5a	2.67	0.67	1.12	2.74
3 ^g	5a	1.60	0.80	0.89	2.32
4	5b	0.43	1.29	1.30	2.77
5	5c	0.54	1.62	1.38	3.26
6	5d	0.32	0.96	2.73	2.69
7	5e	0.65	1.95	1.87	2.85
8 ^f	5e	2.16	0.54	1.08	3.03
9 ^g	5e	2.23	1.11	1.13	2.26
10	6b	0.27	0.80	0.99	3.28
11	6c	0.44	1.32	1.11	2.67
12	7	0.24	0.73	1.35	2.69
1 ^h	5e	0.53	1.60	1.41	2.56
14 ^h	6b	0.19	0.57	0.91	2.92
15 ^h	7	0.17	0.41	1.96	2.75

^a Condition: catalyst (10 μmol , in 1 mL toluene), MMAO, Al/Ti = 4000, temperature of bath = 110 $^\circ\text{C}$, $t = 20$ min, $V_{\text{styrene}} = 30$ mL, aging time = 15 min.^b As the amount of aPS was smaller than that produced in the blank experiments, it was concluded that sPS was afforded exclusively.^c 10^5 g sPS/mol(Ti) h.^d Determined by GPC.^e 10^4 g/mol.^f Polymerization time = 4 h.^g Temperature of bath = 130 $^\circ\text{C}$, $t = 2$ h.^h No catalyst aging.

phenolate could be modified readily by introducing different groups, it provides a potential way to develop thermal stable styrene syndiospecific polymerization catalyst.

Acknowledgements

We are grateful for the financial support from the National Natural Science Foundation of China (nos. 21174159 and 21121062) and Chinese Academy of Sciences.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.molcata.2013.11.032>.

References

- [1] N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, *J. Mol. Catal. A: Chem.* 128 (1998) 167.
- [2] N. Ishihara, T. Seimiya, M. Kuramoto, M. Uoi, *Macromolecules* 19 (1986) 2464.
- [3] A.S. Rodrigues, E. Kirillov, J.F. Carpentier, *Coord. Chem. Rev.* 252 (2008) 2115.
- [4] (a) N. Ishihara, M. Kuramoto, M. Uoi, *Macromolecules* 21 (1988) 3356; (b) J.C.W. Chien, Z. Salajka, *J. Polym. Sci., Part A: Polym. Chem.* 29 (1991) 1253; (c) T.E. Ready, R.O. Day, J.C.W. Chien, M.D. Rausch, *Macromolecules* 26 (1993) 5822; (d) G. Ricci, C. Bosio, L. Porri, *Macromol. Rapid Commun.* 17 (1996) 781; (e) T.E. Ready, J.C.W. Chien, M.D. Rausch, *J. Organomet. Chem.* 519 (1996) 21; (f) Q. Wang, R. Quyoum, D.J. Gillis, M.J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, *Organometallics* 15 (1996) 693; (g) W. Kaminsky, S. Lenk, V. Scholz, H.W. Roesky, A. Herzog, *Macromolecules* 30 (1997) 7647; (h) S.Y. Knjazhanski, G. Cadenas, M. Garcia, C.M. Perez, I.E. Nifant'ev, I.A. Kashulin, P.V. Ivchenko, K. Lyssenko, *Organometallics* 21 (2002) 3094; (i) O. Stojkovic, W. Kaminsky, *Macromol. Chem. Phys.* 205 (2004) 357; (j) M. Erben, J. Merna, S. Hermanova, I. Cisarova, Z. Padelkova, M. Dusek, *Organometallics* 26 (2007) 2735; (k) Y. Luo, S. Chi, J. Chen, *New J. Chem.* 37 (2013) 2675.
- [5] (a) Y. Kim, E. Hong, M.H. Lee, J. Kim, Y. Do, *Organometallics* 18 (1999) 36; (b) Y. Kim, Y. Han, Y. Do, *Organometallics* 21 (2002) 1127; (c) J. Chen, Y.S. Li, J.Q. Wu, *J. Mol. Catal. A: Chem.* 232 (2005) 1; (d) K.-S. Son, R.M. Waymouth, *J. Polym. Sci., Part A: Polym. Chem.* 48 (2010) 1579.
- [6] (a) J. Okuda, E. Masoud, *Macromol. Chem. Phys.* 199 (1998) 543; (b) C. Capacchione, J. Okuda, *J. Am. Chem. Soc.* 125 (2003) 4964; (c) C. Capacchione, A. Proto, J. Okuda, *J. Mol. Catal. A: Chem.* 213 (2004) 137; (d) K. Michiue, M. Onda, H. Tanaka, H. Makio, M. Mitani, T. Fujita, *Macromolecules* 41 (2008) 6289.
- [7] (a) J.C. Flores, J.C.W. Chien, M.D. Rausch, *Organometallics* 14 (1995) 1827; (b) D. Liguori, R. Centore, A. Tuzi, A. Zambelli, *Macromolecules* 36 (2003) 5451; (c) M. Hafeez, W.P. Kretschmer, R. Kempe, *Eur. J. Inorg. Chem.* (2011) 5512; (d) R. Tanaka, P. Viehmann, S. Hecht, *Organometallics* 31 (2012) 4216; (e) Y.Y. Wang, B.X. Li, F.M. Zhu, H.Y. Gao, Q. Wu, *J. Appl. Polym. Sci.* 125 (2012) 121.
- [8] (a) F.M. Zhu, Q.F. Wang, H.M. Li, S.G. Lin, *J. Appl. Polym. Sci.* 79 (2001) 1243; (b) J.H. Kim, S. Yoon, S. Mun, S.H. Kim, J. Lee, Y. Chung, S.H. Kwon, K.S. Lee, C. Lee, Y. Kim, *J. Organomet. Chem.* 696 (2011) 1729.
- [9] (a) Y. Luo, J. Baldamus, Z. Hou, *J. Am. Chem. Soc.* 126 (2004) 13910; (b) A.-S. Rodrigues, E. Kirillov, T. Roisnel, C.W. Lehmann, B. Vuillemin, A. Razavi, J.-F. Carpentier, *Chem. Eur. J.* 13 (2007) 5548; (c) M. Nishiura, T. Mashiko, Z. Hou, *Chem. Commun.* (2008) 2019; (d) X. Fang, X. Li, Z. Hou, J. Assoud, R. Zhao, *Organometallics* 28 (2009) 517; (e) X. Li, M. Nishiura, L. Hu, K. Mori, Z. Hou, *J. Am. Chem. Soc.* 131 (2009) 13870; (f) X. Xu, Y.F. Chen, J. Sun, *Chem. Eur. J.* 15 (2009) 846; (g) L. Perrin, Y. Sarazin, E. Kirillov, J.-F. Carpentier, L. Maron, *Chem. Eur. J.* 15 (2009) 3773; (h) F. Bonnet, C.D.C. Violante, P. Roussel, A. Mortreux, M. Visseaux, *Chem. Commun.* (2009) 3380; (i) L. Perrin, E. Kirillov, J.-F. Carpentier, L. Maron, *Macromolecules* 43 (2010) 6330; (j) D. Liu, Y. Luo, W. Gao, D. Cui, *Organometallics* 29 (2010) 1916; (k) L. Pan, K. Zhang, M. Nishiura, Z. Hou, *Macromolecules* 43 (2010) 9591; (l) F. Guo, M. Nishiura, H. Koshino, Z. Hou, *Macromolecules* 44 (2011) 6335; (m) Y. Pan, W. Rong, Z. Jian, D. Cui, *Macromolecules* 45 (2012) 1248; (n) Z. Jian, D. Cui, Z. Hou, *Chem. Eur. J.* 18 (2012) 2674.
- [10] (a) S.Y. Lee, S.-K. Kim, T.M. Nguyen, J.S. Chung, S.B. Lee, K.Y. Choi, *Macromolecules* 44 (2011) 1385; (b) L. Annunziata, Y. Sarazin, M. Duc, J.-F. Carpentier, *Macromol. Rapid Commun.* 32 (2011) 751.
- [11] (a) J. Liu, H. Ma, J. Huang, Y. Qian, *Eur. Polym. J.* 36 (2000) 2055; (b) D.J. Byun, A. Fudo, A. Tanaka, M. Fujiki, K. Nomura, *Macromolecules* 37 (2004) 5520; (c) K. Nomura, *Dalton Trans.* (2009) 8811; (d) W. Apisuk, N. Suzuki, H.J. Kim, D.H. Kim, B. Kitiyanan, K. Nomura, *J. Polym. Sci., Part A: Polym. Chem.* 51 (2013) 2565; (e) W. Apisuk, B. Kitiyanan, H.J. Kim, D.H. Kim, K. Nomura, *J. Polym. Sci., Part A: Polym. Chem.* 51 (2013) 2581.
- [12] (a) For review, see: C. Redshaw, Y. Tang, *Chem. Soc. Rev.* 41 (2012) 4484; (b) Other examples: W.Q. Hu, X.L. Sun, C. Wang, Y. Gao, Y. Tang, *Organometallics* 23 (2004) 1684; (c) M.L. Gao, C. Wang, X.L. Sun, C.T. Qian, Z. Ma, S. Bu, Y. Tang, *Macromol. Rapid Commun.* 28 (2007) 1511; (d) M.L. Gao, Y. Gu, C. Wang, X.L. Yao, X.-L. Sun, Y. Tang, *J. Mol. Catal. A: Chem.* 1–2 (2008) 62; (e) X.-H. Yang, C.-R. Liu, C. Wang, X.-L. Sun, Y.-H. Guo, X.-K. Wang, Z. Wang, Z. Xie, Y. Tang, *Angew. Chem. Int. Ed.* 48 (2009) 8099; (f) D.-W. Wan, Y.-S. Gao, J.-F. Li, Q. Shen, X.-L. Sun, Y. Tang, *Dalton Trans.* 41 (2012) 4552; (g) D.-W. Wan, Z. Chen, Y.-S. Gao, Q. Shen, X.-L. Sun, Y. Tang, *J. Polym. Sci., Part A: Polym. Chem.* 51 (2013) 2495.
- [13] (a) P. Kamaras, C.C. Michelle, M. Rapta, G.A. Brewer, G.B. Jameson, *J. Am. Chem. Soc.* 116 (1994) 10334; (b) R. Gupta, S. Mukherjee, R. Mukherjee, *J. Chem. Soc. Dalton Trans.* (1999) 4025.
- [14] (a) A. Shah, A. Singh, R.C. Mehrotra, *Polyhedron* 5 (1986) 1285; (b) A.J. Nielson, P. Schwerdtfeger, J.M. Waters, *J. Chem. Soc. Dalton Trans.* (2000) 529.
- [15] CCDC926427 (6b) and CCDC926428 (7) contains the supplementary crystallographic data. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
- [16] S.Z. Hu, Z.H. Zhou, Q.R. Cai, *Acta Phys. Chim. Sin.* 19 (2003) 1073.
- [17] (a) E.Y. Tshuva, S. Groysman, I. Goldberg, M. Kol, *Organometallics* 21 (2002) 662; (b) Y.-C. Hu, C.C. Tsai, W.C. Shih, G.P.A. Yap, T.G. Ong, *Organometallics* 29 (2010) 516; (c) X. Wang, J. Sit, M.M. Sun, Y. Tang, Z. Xie, *Acta Chim. Sin.* 70 (2012) 1909.
- [18] (a) J.C. Vizzini, J.C.W. Chien, C.N. Babu, R.A. Newmark, *J. Polym. Sci., Part A: Polym. Chem.* 32 (1994) 2049; (b) J.-N. Pédeutour, K. Radhakrishnan, H. Cramail, A. Deffieux, *Macromol. Rapid Commun.* 22 (2001) 1095.
- [19] (a) J.C.W. Chien, Z. Salajka, S. Dong, *Macromolecules* 25 (1992) 3199; (b) M.K. Mahanthappa, R.M. Waymouth, *J. Am. Chem. Soc.* 123 (2001) 12093.
- [20] Y.R. Luo, *Comprehensive Handbook of Chemical Bond Energies*, CRC Press, Boca Raton, 2007.