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(ArO)TiR$_3$ complexes for highly syndiospecific styrene polymerization

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ABSTRACT

A kind of (ArO)TiR$_3$ (ArO = 2,6-(R′)$_2$-4-methylphenolate, R′ = Me, ^{t}Bu, CH$_2$SPh, CH$_2$N(^{i}Pr)$_2$, CH$_2$NPh$_2$) complexes was synthesized and characterized. X-ray analysis of **6a** and **7** shows that neither —CH$_2$SPh (**6a**) nor —CH$_2$N(^{i}Pr)$_2$ group (**7**) coordinates to titanium. Large bond angles C(Ar)-O(1)-Ti(1) angel (152.9(2)° in **6a** and 175.33° in **7** indicate that the bond have partial sp-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 (1.11×10^5 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.

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]. CpTiCl$_3$ 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 η^5-cyclopentadienyl derivatives were usually designed to modulate the properties of active species. For example, Okuda disclosed that bis(phenolato)titanium complexes ({(OC$_6$H$_2$-4-Me-6-^{t}Bu)$_2$S}TiX$_2$, X = Cl, O^{i}Pr, C$_5$Me$_5$) were highly active to polymerize styrene syndiospecifically [6a]. FI catalyst based on phenoxy-imine/MAO 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-Bu$_2$C$_4$H$_2$N)Sc(CH$_2$C$_6$H$_4$NMe$_2$-O)$_2$/[Ph$_3$C][B(C$_6$F$_5$)$_4$] developed by Hou and coworkers afforded high molecular weight syndiotactic polystyrene in high activity [9c]. Mono(indenyl)-Sc-dialkyl/[Ph$_3$C][B(C$_6$F$_5$)$_4$] developed by Chen et al. was extremely efficient in producing syndiopolystyrene [9f]. Recently, a monomeric pentamethylcyclopentadienyltitanatranes 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) mol styrene h). The steric bulkiness in tetradentate ligands has great influence on the polymerization and the activity drastically decreased in the case of Cp*Ti(OCH$_2$CH$_2$)$_3$N (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 ArOTiX$_3$ (X = NMe$_2$, Cl, CH$_2$Ph) 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 1.11×10^5 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 CaH_2 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). ^{1}H NMR and ^{13}C 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). ^{13}C NMR data for polymers were obtained using $CDCl_3$ 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%). ^{1}H NMR (300 MHz, $CDCl_3$): δ (ppm) = 7.35–7.19 (m, 10H), 6.79 (s, 2H), 6.45 (s, 1H), 4.14 (s, 4H), 2.11(s, 3H). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{21}H_{20}OS_2$ (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%) ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 (Ph_2N). HRMS (EI): calcd for $C_{33}H_{30}N_2O$ (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%). ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{21}H_{38}N_2O$ (M^+) 334.2984; found 334.2984.

[2,6-Bis(phenylthiomethyl)-4-methylphenolate]Ti(IV)Cl_3(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 $TiCl_4(THF)_2$ (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%). ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{25}H_{26}Cl_3O_2S_2Ti$ (576.83): C 52.05, H 4.54; Found: C 51.77, H 4.62.

[2,6-Bis((diisopropylamino)methyl)-4-methylphenolate Ti(IV)Cl_3(THF)] (**5b**). A same procedure as that for the preparation of **5a** was used. Yield dark-red solid, 2.90 g (61%). ^{1}H NMR (300 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): ^{13}C NMR (100 MHz, $CDCl_3$): 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 $C_{25}H_{44}Cl_3N_2O_2Ti$ (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)Cl_3(THF)] (**5e**). To a solution of $TiCl_4$ (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%) ^{1}H NMR (400 MHz, $CDCl_3$): 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). ^{13}C NMR (75 MHz, $CDCl_3$): 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 $C_{15}H_{23}Cl_3O_2Ti$ (389.57): C 46.25, H 5.95; Found: C 45.86, H 6.30.

[2,6-Bis(phenylthiomethyl)-4-methyl-phenolate Ti(IV)$(NMe_2)_3$] (**6a**). To a solution of $Ti(NMe_2)_4$ (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%). ^{1}H NMR (400 MHz, C_6D_6): 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). ^{13}C NMR (100 MHz, C_6D_6): 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 $C_{27}H_{37}N_3OS_2Ti$ (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)$(NMe_2)_3$ (**6b**). The same procedure as that for the preparation of **6a** was used. Yellow crystal 0.49 g (yield: 76%). ^{1}H NMR (300 MHz, C_6D_6): 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). ^{13}C NMR (100 MHz, C_6D_6): 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 $C_{39}H_{47}N_5OTi$ (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)$(NMe_2)_3$ (**6c**). The same procedure as that for the preparation of **6a** was used. Yield yellow crystal, 0.37 g (92.6%). ^{1}H NMR (400 MHz, C_6D_6): δ (ppm) = 7.21 (s, 2H), 3.08 (s, 18H), 2.31 (s, 3H), 1.57 (s, 18H). ^{13}C NMR (100 MHz, C_6D_6): δ (ppm) = 162.3, 139.6, 127.7, 125.9, 45.4, 35.2, 30.5, 21.5. Anal. Calcd for $C_{21}H_{41}N_3OTi$ (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)Bn_3] (**7**). To a solution of $TiBn_4$ (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