Copolymerization of Ethylene with Cycloolefins by Titanium Complexes Containing Tridentate [O^-NS^R] Ligands

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ABSTRACT: A family of titanium complexes of the general formula [N-(3,5-di-*tert*-butylsalicylidene)-2-alkylsulfanylanilinato]Ti(IV)Cl_3 **5a–f** was prepared from the reaction of $TiCl_4$ with the potassium salts of the corresponding ligands. These complexes were fully characterized by various spectroscopic techniques and elemental analyses. The molecular structures of **5b** and **5e** were further confirmed by single-crystal X-ray analyses. Complexes **5a–f** (except for **5c**) exhibited good to high catalytic activities in ethylene copolymerization with cycloolefins such as norbornene, cyclopentene, dicyclopentadiene in the presence of modified methylaluminoxane. The reaction conditions and the steric hindrance of the alkyl substituents on sulfur atom in the precatalysts influenced strongly the copolymerization behaviors and the structures of the resultant copolymers. Complex **5c** with bulky *tert*-butylthio sidearm showed both low catalytic activity and comonomer incorporation ratio. The *n*-alkylthio complexes **5a**, **5d–f** all exhibited good ethylene copolymerization capabilities with cycloolefins, which is superior to the corresponding phenylthio complex **5g**. © 2008 Wiley Periodicals, Inc. J Polym Sci Part A: Polym Chem 46: 2807–2819, 2008
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INTRODUCTION

In recent years, the development of non-metallocene polymerization catalysts has attracted considerable attention for the quest for ever-higher catalyst productivity and novel polymer materials.[1–8] Group 4 metal complexes [O^-N]$_2MCl_2$ (O^-N = phenoxy-imine)[3–8] proved to be an excellent precatalysts for olefin polymerizations, including ethylene living polymerization,[4,5] highly syndiospecific propene living polymerization,[6] living copolymerization of ethylene with α-olefin,[7] and the synthesis of functional block copolymers.[8] Recently, we reported several [O^-NX^{Ar}] $TiCl_3$ complexes where X = O, S, Se, and P (Chart 1) and investigated their behaviors as olefin polymerization catalysts.[9] It was found that some of these complexes were highly active for ethylene polymerization and copolymeriza-

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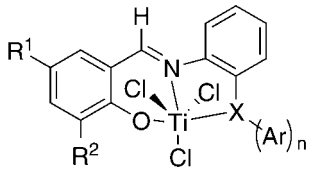


X = O, S, Se, n = 1 and X = P, n = 2
5g $R^1 = R^2 = {}^t$Bu, X = S, Ar = Ph

Chart 1

tion with α-olefin upon activation with modified methylaluminoxane (MMAO). The activity and the copolymerization capability strongly depended on the sidearm group X^{Ar}.[10–12]

Copolymers of ethylene with cycloolefin are a promising class of thermoplastics, ranging from highly crystalline solids through amorphous glasses to thermoplastic elastomers. The precise physical properties of these materials are dependent upon the frequency, region- and stereo-selectivity of comonomer incorporation, which are in turn dictated by both the catalyst structure and polymerization conditions.[13] In this connection, we investigated the copolymerization of ethylene with cycloolefins using $[NOX^{Ar}]TiCl_3$ complexes as the precatalysts and found that they only exhibited moderate activities presumably due to the steric reasons.[9(b,c)] To overcome this problem and to improve the catalyst activity, we designed and synthesized several titanium complexes bearing alkylthio functional groups $[O^-NX^R]TiCl_3$ (R = alkyl) (**5a–f**) by considering the steric/electronic nature of alkyl and aryl substituents. It was found that methylthio complex **5a** was an excellent catalyst for ethylene–norbernene copolymerization with an activity of 2.03×10^6 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}, which is about 10 times more active than the corresponding arylthio counterparts (**5g**, Chart 1).[14] We then extended our research to include complexes **5b–5f** and other cycloolefins. In this article, we report a full account of our study on the synthesis and structural characterization of titanium complexes $[O^-NX^R]TiCl_3$ (R = alkyl) (**5a–f**), the copolymerization of ethylene with cycloolefins as well as the characterization of the resultant copolymers.

EXPERIMENTAL

Materials

All manipulations of air- and moisture-sensitive compounds were carried out under an atmosphere of dry nitrogen using standard Schlenk or cannula techniques, or in a glovebox. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 300 spectrometer. All chemical shifts were reported in δ units with reference to internal TMS (0.00 ppm). Infrared spectra were obtained from KBr pellets on a Perkin-Elmer 983 spectrometer. Mass spectra were obtained using the direct insertion probe method on a HP5989A instrument operating at 70 eV. High-resolution mass spectra (HRMS) were measured by a Finnigan Perkin–Elmer 241MC instrument. Elemental analyses were performed on a Vario EL III instrument. Methylene chloride was distilled over CaH_2 prior to use. All other organic solvents were freshly distilled from sodium benzophenone ketyl immediately prior to use. Cyclopentene (CPE) and norbornene (NBE) were distilled over sodium, and dicyclopentadiene (DCPD) was distilled over CaH_2. MMAO was purchased from Akzo Nobel as a 7 wt % solution in toluene. Polymerization-grade ethylene was purified before use. Deuterated solvents were dried using standard procedures and stored in the glovebox. Compounds **2a**,[14] **2b–d**,[15] **3a–d**,[9] (c)[14] and **5g**[9(b,c)] were prepared according to literature methods. Other chemicals were used as received unless otherwise noted. X-ray crystallographic data was collected at 293 K on a Bruker SMART 1000 CCD diffractometer using Mo Kα radiation. Further details were included in the Supporting Information.

Synthesis of 2-*n*-Octylthionitrobenzene (2e)

A solution of 2-chloronitrobezene (7.88 g, 50 mmol), 1-octanethiol (**1e**; 8.05 g, 9.6 mL, 55 mmol), and NaOH (2.20 g, 55 mmol) in EtOH (25 mL) was stirred at room temperature for 4 h. After removal of EtOH under vacuum, water (80 mL) was added and the resulting solution was extracted with CH_2Cl_2 (50 mL four times). The combined organic solutions were dried over anhydrous Na_2SO_4 and passed through a silica gel plug. After removal of the solvent, the residue was subjected to column chromatographical separation (CH_2Cl_2/petroleum = 1:6) to give **2e** as a yellow liquid (9.72 g, 73%).

^{1}H NMR ($CDCl_3$): δ 8.18 (dd, J = 8.1, 1.5 Hz, 1 H, Ar—*H*), 7.58–7.52 (m, 1 H, Ar—*H*), 7.41 (dd, J = 8.1, 1.5 Hz, 1 H, Ar—*H*), 7.25–7.20 (m, 1 H, Ar—*H*), 2.95 (t, J = 7.2 Hz, 2 H, SCH_2), 1.78–1.67 (m, 2 H, CH_2), 1.53–1.40 (m, 2 H, CH_2), 1.39–1.19 (m, 8 H, CH_2), 0.88 (t, J = 6.9

Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 145.7, 138.3, 133.3, 126.4, 125.9, 124.1 (Ar—*C*), 32.2, 31.6, 29.0, 28.9(9), 28.9(8), 27.7, 22.5, 14.0. IR (KBr, cm^{-1}): ν 3086 (w), 2927 (vs), 2855 (s), 1594 (s), 1566 (s), 1514 (vs), 1456 (m), 1436 (w), 1337 (vs), 1305 (s), 733 (s). Anal. Calcd for $C_{14}H_{21}NO_2S$: C, 62.89; H, 7.92; N, 5.24. Found: C, 62.96; H, 7.90; N, 5.28. EI-MS (*m/z* (%)): 43 (100), 267 (4) [M^+].

Synthesis of 2-*n*-Octadecylthionitrobenzene (2f)

A solution of 2-chloronitrobezene (7.88 g, 50 mmol), 1-octadecanethiol (**1f**; 15.76 g, 55 mmol), and NaOH (2.20 g, 55 mmol) in EtOH (80 mL) was stirred at room temperature for 4 h to give a yellow viscous suspension. After addition of water (200 mL), the precipitate was collected by filtration and washed with water, followed by EtOH. The crude product was purified by column chromatography (ethyl acetate/petroleum = 1:60) to give **2f** as a yellow solid (14.46 g, 71%). Mp: 58–59 °C.

^{1}H NMR ($CDCl_3$): δ 8.20 (dd, J = 8.4, 1.2 Hz, 1 H, Ar—*H*), 7.58–7.51 (m, 1 H, Ar—*H*), 7.41 (d, J = 8.1 Hz, 1 H, Ar—*H*), 7.27–7.20 (m, 1 H, Ar—*H*), 2.95 (t, J = 7.5 Hz, 2 H, SCH_2), 1.79–1.68 (m, 2 H, CH_2), 1.53–1.40 (m, 2 H, CH_2), 1.25 (s, 28 H, CH_2), 0.88 (t, J = 6.9 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 145.9, 138.4, 133.4, 126.4, 126.1, 124.2 (Ar—*C*), 32.3, 31.9, 29.7, 29.6, 29.5, 29.4, 29.3, 29.2, 29.1, 27.8, 22.7, 14.1. IR (KBr, cm^{-1}): ν 2956 (w), 2916 (vs), 2851 (s), 1599 (m), 1561 (m), 1514 (s), 1469 (m), 1332 (s), 1305 (s), 729 (s). Anal. Calcd for $C_{24}H_{41}NO_2S$: C, 70.71; H, 10.14; N, 3.44. Found: C, 70.61; H, 10.29; N, 3.07. EI-MS (*m/z* (%)): 57 (100), 407 (1) [M^+].

Synthesis of 2-*n*-Octylthioaniline (3e)

An EtOH (20 mL) solution of 2-*n*-octylthionitrobenzene (**2e**; 8.46 g, 32 mmol) was slowly added to a suspension of zinc dust (11.37 g, 174 mmol) in EtOH (20 mL) containing AcOH (5 mL) at room temperature, and the mixture was stirred for 0.5 h. The resulting solution was filtered through diatomite, followed by washing with ether. The filtrate was added into water (180 mL) and the organic phase was separated. The aqueous solution was extracted with ether (60 mL thrice). The combined organic solutions were washed with water, dried over Na_2SO_4, and passed through a silica gel plug. Removal of the solvents under vacuum gave **3e** as a yellow liquid (6.58 g, 88%).

^{1}H NMR ($CDCl_3$): δ 7.36 (d, J = 7.8 Hz,1 H, Ar—*H*), 7.10 (t, J = 7.8 Hz, 1 H, Ar—*H*), 6.74–6.66 (m, 2 H, Ar—*H*), 4.33 (s, 2 H, NH_2), 2.73 (t, J = 7.2 Hz, 2 H, SCH_2), 1.61–1.51 (m, 2 H, CH_2), 1.44–1.20 (m, 10 H, CH_2), 0.87 (t, J = 6.6 Hz, 3 H, CH_3).

Synthesis of 2-*n*-Octadecylthioaniline (3f)

A solution of 2-*n*-octadecylthionitrobenzene (**2f**; 12.73 g, 31 mmol) in a mixed solvent of EtOH (60 mL) and CH_2Cl_2 (60 mL) was slowly added to a suspension of zinc dust (11.23 g, 172 mmol) in EtOH (20 mL) containing AcOH (5 mL) at room temperature, and the mixture was stirred for 1 h. The resulting solution was filtered through diatomite, followed by washing with CH_2Cl_2. The filtrate was added into water (350 mL), and the organic phase was separated. The aqueous solution was extracted with CH_2Cl_2 (120 mL thrice). The combined organic solutions were washed with water, dried over Na_2SO_4, and passed through a silica gel plug. Removal of the solvents under vacuum gave **3f** as a yellow solid (11.45 g, 97%). Mp: 38–39 °C.

^{1}H NMR ($CDCl_3$): δ 7.36 (dd, J = 7.8, 1.5 Hz, 1 H, Ar—*H*), 7.12–7.05 (m, 1 H, Ar—*H*), 6.72–6.64 (m, 2 H, Ar—*H*), 4.31 (brs, 2 H, NH_2), 2.72 (t, J = 7.5 Hz, 2 H, SCH_2), 1.60–1.50 (m, 2 H, CH_2), 1.43–1.11 (m, 30 H, CH_2), 0.88 (t, J = 6.6 Hz, 3 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 148.0, 135.6, 129.3, 118.3, 114.7 (Ar—*C*), 34.8, 31.9, 29.7, 29.6, 29.5, 29.4, 29.2, 28.7, 22.7, 14.1. IR (KBr, cm^{-1}): ν 3402 (s), 3325 (s), 3061 (w), 2952 (w), 2917 (vs), 2849 (s), 2917 (vs), 2849 (s), 1624 (s), 1575 (m), 1483 (s), 1471 (s), 1445 (m), 1292 (m), 741 (s), 718 (s). Anal. Calcd for $C_{24}H_{43}NS$: C, 76.33; H, 11.48; N, 3.71. Found: C, 76.42; H, 11.76; N, 3.33. EI-MS (*m/z* (%)):125 (100), 377 (48) [M^+].

Synthesis of *N*-(3,5-di-*tert*-butylsalicylidene)-2-*n*-propylsulfanylaniline (4d)

To a solution of 3,5-di-*tert*-butylsalicyaldehyde (3.87 g, 17 mmol) and **3d** (2.78 g, 17 mmol) in ethanol (30 mL) was added AcOH (0.5 mL) at room temperature. The mixture was heated to reflux with stirring for 12 h, cooled to room temperature, and then kept at −30 °C overnight to afford **4d** as a yellow solid (5.04 g, 79%). Mp: 109–110 °C.

^{1}H NMR ($CDCl_3$): δ 13.46 (s, 1 H, O*H*), 8.60 (s, 1 H, C*H*N), 7.46 (d, J = 2.7 Hz, 1 H, Ar—*H*), 7.36–7.32 (m, 1 H, Ar—*H*), 7.24–7.19 (m, 3 H, Ar—*H*), 7.14–7.10 (m, 1 H, Ar—*H*), 2.90 (t, J = 7.2 Hz, 2 H, SCH_2), 1.79–1.67 (m, 2 H, CH_2), 1.49 (s, 9 H, C(CH_3)$_3$), 1.33 (s, 9 H, C(CH_3)$_3$), 1.05 (t, J = 7.2 Hz, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 163.4 (*C*H=N), 158.4, 147.1, 140.4, 137.0, 132.9, 128.2, 127.4, 126.83, 126.79, 125.9, 118.3, 118.0 (Ar—*C*), 35.1, 34.2, 34.1, 31.4, 29.4, 22.3, 13.6. IR (KBr, cm^{-1}): ν 2960 (vs), 2869 (w), 1612 (s), 1591 (w), 1562 (m), 1462 (s), 1439 (m), 1171 (m), 746 (m). Anal. Calcd for $C_{24}H_{33}NOS$: C, 75.15; H, 8.67; N, 3.65. Found: C, 74.90; H, 8.62; N, 3.40. EI-MS (*m/z* (%)): 57 (100), 383 (60) [M^+].

Synthesis of *N*-(3,5-di-*tert*-butylsalicylidene)-2-*tert*-butylsulfanylaniline (4c)

This compound was prepared as a yellow solid from 3,5-di-*tert*-butylsalicylaldehyde (1.22 g, 5 mmol), **3c** (0.95 g, 5 mmol) and AcOH (0.3 mL) using the same procedures as those for **4d** (1.48 g, 71%). Mp: 99–101 °C.

^{1}H NMR ($CDCl_3$): δ 13.91 (s, 1 H, O*H*), 8.59 (s, 1 H, C*H*N), 7.68–7.65 (m, 1 H, Ar—*H*), 7.46–7.41 (m, 2 H, Ar—*H*), 7.26–7.21 (m, 3 H, Ar—*H*), 1.49 (s, 9 H, ArC(CH_3)$_3$), 1.33 (s, 9 H, ArC(CH_3)$_3$), 1.30 (s, 9 H, SC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 163.6 (*C*H=N), 158.5, 152.6, 140.2, 139.7, 137.1, 130.3, 128.1, 127.9, 126.7, 126.3, 118.6, 118.3 (Ar—*C*), 47.7, 35.2, 34.1, 31.5, 31.1, 29.4. IR (KBr, cm^{-1}): ν 2960 (vs), 2903 (w), 1617 (s), 1575 (w), 1470 (s), 1361 (m), 1168 (s), 756 (s). HRMS calcd for $C_{25}H_{35}NOS$: 397.2439, found: 397.2447. EI-MS (*m/z* (%)): 340 (100), 397 (51) [M^+].

Synthesis of *N*-(3,5-di-*tert*-butylsalicylidene)-2-*n*-octylsulfanylaniline (4e)

This compound was prepared as a yellow solid from 3,5-di-*tert*-butylsalicylaldehyde (5.60 g, 24 mmol), **3e** (5.70 g, 24 mmol) and AcOH (1.0 mL) using the same procedures as those for **4d** (5.53 g, 51%). Mp: 57–58 °C.

^{1}H NMR ($CDCl_3$): δ 13.49 (s, 1 H, O*H*), 8.59 (s, 1 H, C*H*N), 7.47 (d, J = 1.8 Hz, 1 H, Ar—*H*), 7.34–7.29 (m, 1 H, Ar—*H*), 7.23–7.09 (m, 4 H, Ar—*H*), 2.90 (t, J = 7.2 Hz, 2 H, SCH_2), 1.74–1.63 (m, 2 H, CH_2), 1.50 (s, 9 H, C(CH_3)$_3$), 1.55–1.37 (m, 2 H, CH_2), 1.33 (s, 9 H, C(CH_3)$_3$), 1.26 (s, 8 H, CH_2), 0.87 (t, J = 6.6 Hz, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 163.4 (*C*H=N), 158.4, 147.1, 140.4, 137.0, 133.0, 128.1, 127.3, 126.82, 126.79, 125.9, 118.3, 118.0 (Ar—*C*), 35.1, 34.1, 32.2, 31.8, 31.4, 29.4, 29.1, 29.0, 28.9, 22.6, 14.1. IR (KBr, cm^{-1}): ν 2958 (s), 2923 (s), 2853 (m), 1613 (s), 1590 (m), 1574 (m), 1561 (m), 1466 (s), 1440 (m), 750 (m). Anal. Calcd for $C_{29}H_{43}NOS$: C, 76.77; H, 9.55; N, 3.09. Found: C, 77.08; H, 9.80; N, 3.19. EI-MS (*m/z*(%)): 57 (100), 454 (24) [$(M+1)^+$].

Synthesis of *N*-(3,5-di-*tert*-butylsalicylidene)-2-*n*-octadecylsulfanylaniline (4f)

To a solution of 3,5-di-*tert*-butylsalicyaldehyde (5.89 g, 25 mmol) and **3f** (9.54 g, 25 mmol) in ethanol (70 mL) was added AcOH (1.0 mL) at room temperature. The mixture was heated to reflux with stirring for 21 h, cooled to room temperature, and kept at −30°C overnight to afford a yellow solid as a crude product. Column chromatographical separation on silica gel (CH_2Cl_2/petroleum = 1:100) gave **4f** as a yellow solid (9.76 g, 65%). Mp: 45–46 °C.

^{1}H NMR ($CDCl_3$): δ 13.48 (s, 1 H, O*H*), 8.59 (s, 1 H, C*H*N), 7.47 (s, 1 H, Ar—*H*), 7.36–7.27 (m, 1 H, Ar—*H*), 7.26–7.08 (m, 4 H, Ar—*H*), 2.90 (t, J = 7.2 Hz, 2 H, SCH_2), 1.76–1.62 (m, 2 H, CH_2), 1.50 (s, 9 H, C(CH_3)$_3$), 1.50–1.39 (m, 2 H, CH_2), 1.33 (s, 9 H, C(CH_3)$_3$), 1.25 (s, 28 H, CH_2), 0.88 (t, J = 6.0 Hz, 3 H, CH_2CH_3). ^{13}C NMR ($CDCl_3$): δ 163.4 (*C*H=N), 158.4, 147.2, 140.4, 137.1, 133.1, 128.1, 127.4, 126.83, 126.79, 125.9, 118.4, 118.0 (Ar—*C*), 35.1, 34.1, 32.3, 31.9, 31.5, 29.7, 29.6, 29.5, 29.4(4), 29.4(0), 29.2, 29.0, 28.9, 22.7, 14.1. IR (KBr, cm^{-1}): ν 2953 (s), 2918 (vs), 2851 (s), 1614 (s), 1592 (w), 1575 (m), 1564 (m), 1471 (s), 1438 (m), 748 (m). HRMS calcd for $C_{39}H_{64}NOS^+$(Maldi): 594.4703, found: 594.4697 ($M+H^+$). EI-MS (*m/z*(%)): 57 (100), 594 (42) [$(M+1)^+$].

Synthesis of [N-(3,5-di-*tert*-butylsalicylidene)-2-*n*-propylsulfanylanilinato]Ti(IV)Cl_3 (5d)

To a suspension of KH (0.122 g, 3.0 mmol) in THF (10 mL) was added a solution of **4d** (1.078 g, 2.8 mmol) in THF (10 mL) at −78 °C. The resulting suspension was warmed to room temperature and stirred for 2 h. After the solvent was removed under vacuum, toluene (40 mL) was added to the residue to give a yellow solution. It was then added dropwise to a solution of $TiCl_4$ (0.639 g, 3.4 mmol) in toluene (10 mL) at room temperature, and the mixture was stirred

overnight. The precipitate was filtered off and washed with CH_2Cl_2 (30 mL twice). The combined organic solutions were concentrated under vacuum to about 30 mL and then kept at −30 °C overnight to afford **5d** as reddish crystals (0.920 g, 61%).

^{1}H NMR ($CDCl_3$): δ 8.79 (s, 1 H, C*H*N), 7.75 (d, J = 1.8 Hz, 1 H, Ar—*H*), 7.68 (dd, J = 7.8, 1.2 Hz, 1 H, Ar—*H*), 7.56–7.41 (m, 4 H, Ar—*H*), 3.54 (brs, 2 H, SCH_2), 2.12–1.99 (m, 2 H, CH_2CH$_3$), 1.55 (s, 9 H, C(CH_3)$_3$), 1.37 (s, 9 H, C(CH_3)$_3$), 1.16 (t, J = 7.5 Hz, 3 H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): δ 163.5 (*C*H=N), 161.0, 150.7, 147.5, 136.3, 134.3, 133.1, 131.4, 131.1, 130.0, 128.7, 127.5, 119.3 (Ar—*C*), 47.7, 35.4, 34.8, 31.2, 29.8, 21.7, 13.4. IR (KBr, cm^{-1}): ν 2961 (s), 2905 (w), 2868 (w), 1591 (m), 1544 (s), 1475 (m), 757 (s). Anal. Calcd for $C_{24}H_{32}Cl_3NOSTi$: C, 53.70; H, 6.01; N, 2.61. Found: C, 53.82; H, 6.11; N, 2.72.

Synthesis of [*N*-(3,5-di-*tert*-butylsalicylidene)-2-*tert*-butylsulfanylanilinato]Ti(IV)Cl$_3$ (5c)

This complex was prepared as a red solid from KH (0.103 g, 2.6 mmol), **4c** (0.946 g, 2.4 mmol) and $TiCl_4$ (0.552 g, 2.9 mmol) using the same procedures reported for **5d**: yield 0.924 g (70%).

^{1}H NMR ($CDCl_3$): δ 8.84 (s, 1 H, C*H*N), 7.78–7.72 (m, 2 H, Ar—*H*), 7.60–7.53 (m, 2 H, Ar—*H*), 7.46–7.40 (m, 2 H, Ar—*H*), 1.61 (s, 9 H, SC(CH_3)$_3$), 1.54 (s, 9 H, ArC(CH_3)$_3$), 1.38 (s, 9 H, ArC(CH_3)$_3$). ^{13}C NMR ($CDCl_3$): δ 164.0 (*C*H=N), 162.0, 152.8, 147.3, 136.3, 135.1, 133.3, 131.7, 130.6, 129.1, 127.5, 127.2, 119.5, (Ar—*C*), 57.9, 35.4, 34.8, 31.2, 29.8, 29.5. IR (KBr, cm^{-1}): ν 2961 (s), 2907 (w), 2866 (w), 1591 (m), 1543 (s), 1464 (m), 1364 (m), 1248 (m), 763 (m). Anal. Calcd for $C_{25}H_{34}Cl_3NOSTi$: C, 54.51; H, 6.22; N, 2.54. Found: C, 54.80; H, 6.67; N, 2.62.

Synthesis of [*N*-(3,5-di-*tert*-butylsalicylidene)-2-*n*-octylsulfanylanilinato]Ti(IV)Cl$_3$ (5e)

This complex was prepared as a red solid from KH (0.140 g, 3.5 mmol), **4e** (1.466 g, 3.2 mmol) and $TiCl_4$ (0.742 g, 3.9 mmol) using the same procedures reported for **5d**: yield 1.446 g (74%). X-ray-quality crystals were obtained from recrystallization in dry toluene.

^{1}H NMR ($CDCl_3$): δ 8.78 (s, 1 H, C*H*N), 7.75 (d, J = 2.4 Hz, 1 H, Ar—*H*), 7.70–7.66 (m, 1 H, Ar—*H*), 7.56–7.42 (m, 4 H, Ar—*H*), 3.47 (brs, 2 H, SCH_2), 2.08–1.96 (m, 2 H, CH_2), 1.55–1.47 (m, 2 H, CH_2), 1.55 (s, 9 H, C(CH_3)$_3$), 1.37 (s, 9 H, C(CH_3)$_3$), 1.36–1.22 (m, 8 H, CH_2), 0.88 (t, J = 6.6 Hz, 3 H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): δ 163.5 (*C*H—N), 161.0, 150.7, 147.5, 136.3, 134.3, 133.0, 131.4, 131.1, 130.0, 128.7, 127.4, 119.3 (Ar—*C*), 46.0, 35.3, 34.7, 31.7, 31.2, 29.7, 29.1, 29.0, 28.7, 28.0, 22.6, 14.1. IR (KBr, cm^{-1}): ν 2960 (s), 2924 (s), 2858 (m), 1593 (m), 1558 (m), 1545 (s), 1463 (m), 1433 (w), 876 (m), 761 (s). Anal. Calcd for $C_{29}H_{42}Cl_3NOSTi$: C, 57.39; H, 6.97; N, 2.31. Found: C, 56.85; H, 7.03; N, 2.28.

Synthesis of [*N*-(3,5-di-*tert*-butylsalicylidene)-2-*n*-octadecylsulfanylanilinato]Ti(IV)Cl$_3$ (5f)

This complex was prepared as a red solid from KH (0.146 g, 3.6 mmol), **4f** (2.002 g, 3.4 mmol) and $TiCl_4$ (0.759 g, 4.0 mmol) using the same procedures reported for **5f**: yield 1.963 g (78%).

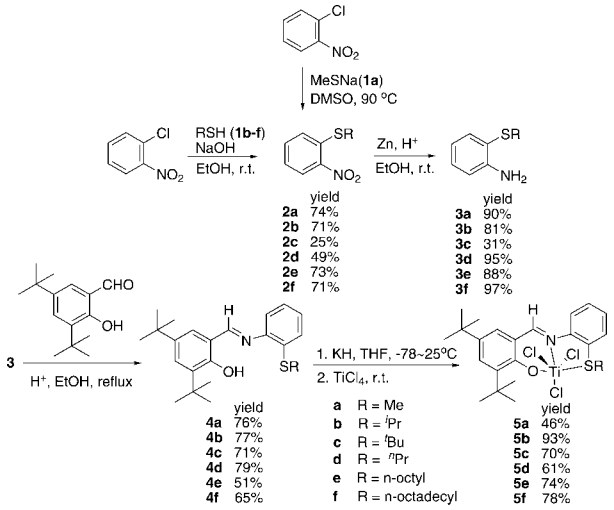
^{1}H NMR ($CDCl_3$): δ 8.79 (s, 1 H, C*H*N), 7.75 (d, J = 1.8 Hz, 1 H, Ar—*H*), 7.67 (dd, J = 7.2, 1.2 Hz, 1 H, Ar—*H*), 7.56–7.41 (m, 4 H, Ar—*H*), 3.45 (brs, 2 H, SCH_2), 2.08–1.95 (m, 2 H, CH_2), 1.57–1.45 (m, 2 H, CH_2), 1.55 (s, 9 H, C(CH_3)$_3$), 1.45–1.23 (m, 28 H, CH_2), 1.37 (s, 9 H, C(CH_3)$_3$), 0.88 (t, J = 6.9 Hz, 3 H, CH$_2$CH_3). ^{13}C NMR ($CDCl_3$): δ 163.5 (*C*H=N), 161.0, 150.7, 147.5, 136.2, 134.2, 133.0, 131.4, 131.1, 130.0, 128.7, 127.4, 119.3 (Ar—*C*), 46.0, 35.3, 34.7, 31.9, 31.2, 29.7, 29.6(5), 29.6(0), 29.5, 29.4, 29.3, 29.0, 28.7, 28.0, 22.6, 14.1. IR (KBr, cm^{-1}): ν 2961 (m), 2922 (s), 2851 (s), 1593 (m), 1558 (m), 1545 (s), 1465 (m), 876 (m), 761 (s). Anal. Calcd for $C_{39}H_{62}Cl_3NOSTi$: C, 62.69; H, 8.36; N, 1.87. Found: C, 62.96; H, 8.56; N, 1.93.

General Procedure of Ethylene–Cycloolefins Copolymerization

A flame-dried Schlenk flask was charged with ethylene and was heated at a desired temperature in an oil bath. A desired amount of freshly distilled toluene was transferred into the flask, and saturated with ethylene. Comonomer and MMAO were injected into the flask in sequence via a syringe, and the mixture was stirred for 5 min. When a toluene solution of the catalyst precursor was added through a syringe, the copolymerization was started. After a desired time, the copolymerization was quenched with acidified ethanol (or acidified methanol), and poured into a large amount of acidified ethanol (300 mL, 10 vol % HCl in ethanol) (or acidified methanol). The precipitated copolymer was collected, washed with ethanol (or methanol), and then dried at 50 °C under vacuum till a constant weight.

Epoxidation of Poly(ethylene-*co*-dicyclopentadiene)

The epoxidation was performed according to the literature.[16] About 200 mg of the copolymer (Table 6, entry 1) and 40 mL of toluene were added to a 100-mL flask under N_2 atmosphere. The reaction mixture was heated at 55 °C with stirring until the copolymer was completely dissolved. A toluene solution (20 mL) of *m*-chloroperbenzoic acid (0.25 g, 1.46 mmol) was added dropwise. The mixture was then stirred at 55 °C for 3 h. The resulting solution was poured into methanol (300 mL). The precipitated copolymer was collected by filtration and dried in vacuo at 60 °C to a constant weight (206 mg). NMR analyses indicated a complete epoxidation of the olefinic groups (see support information).



Scheme 1

Copolymer Characterization

The NMR data of poly(ethylene-*co*-dicyclopentadiene) were recorded by dissolving the samples in $CDCl_3$ at 50 °C. The ^{13}C NMR data of poly (ethylene-*co*-norbornene/CPE) were recorded by dissolving the samples in (D_4)-*o*-dichlorobenzene at 110 °C. Molecular weights (M_w and M_n) and polydispersities were determined on a Waters alliance GPC 2000 series at 135 °C using a polystyrene calibration. 1,2,4-Trichlorobenzene was employed as a solvent at a flow rate of 1.0 mL/min. The DSC measurements were performed on a Perkin-Elmer Pyris 1 Differential Scanning Calorimetry at a heating rate of 10 °C/min from −80 °C to 200 °C. The reported values originated from the second heating scan.

RESULTS AND DISCUSSION

Synthesis and Characterization of Titanium Complexes

The synthetic routes to complexes **5a–f** are shown in Scheme 1. Reaction of 2-chloronitrobenzene with 1 equivalent of sodium thiomethoxide in DMSO at 90 °C gave 2-methylthionitrobenzene **2a**.[14] Treatment of 2-chloronitrobenzene with 1.1 equivalent of alkylthiol (**1b–f**) and NaOH at room temperature afforded nitrobenzene derivatives (**2b–f**) that were then reduced to the corresponding anilines **3** by zinc dust in the presence of glacial acetic acid. Condensation reaction of 3,5-di-*tert*-butylsalicylaldehyde with 1 equivalent of 2-alkylthiolaniline (**3a–f**) in acetic acid gave the phenoxy-imine [O^-NS^R] tridentate ligands (**4a–f**) in 51–79% yields. After deprotonation by 1 equiv. of KH in THF, the resultant potassium salts reacted with 1.2 equiv of $TiCl_4$ at room temperature in toluene to give the desired titanium trichloride complexes (**5a–f**) in 46–93% yields. Noticeably, complexes with longer alkyl chains such as **5e** and **5f** were found to be very thermally stable, and decomposition was not observed in toluene under nitrogen atmosphere at room temperature after 5 months.

All complexes were fully characterized by ^1H and ^{13}C NMR, IR, and elemental analyses. The unique imine proton chemical shift $\delta_{CH=N}$ was observed at about 8.6 ppm in **4a–f**, which was downfield shifted to about 8.8 ppm upon complexation with the Ti(IV) ion in complexes **5a–f**. The SCH_n proton chemical shift δ_{SCH_n} observed in complexes **5a–f** was downfield shifted by about 0.6 ppm in comparison to the corresponding ligands **4a–f**, suggesting that both N and S atoms coordinate to the titanium.

The molecular structures of complexes **5b** and **5e** were further confirmed by single-crystal X-ray analyses. Figure 1 shows the representative structure of **5e.** The Ti atom is bonded to three chlorine atoms, one sulfur, one nitrogen, and one oxygen atom in a distorted-octahedral geometry with the chlorine atoms in a *mer* disposition.

Ethylene–Norbornene Copolymerization

Several elegant catalysts for the copolymerization of ethylene with NBE have been documented in literature.[17] Our complexes (except

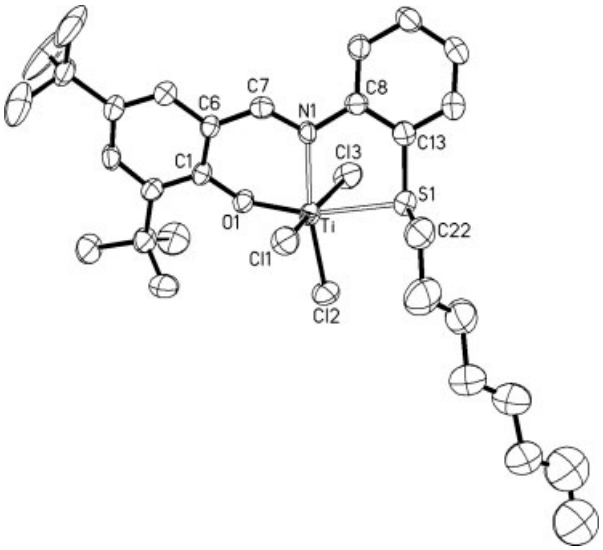


Figure 1. Molecular structure of **5e**. Selected bond lengths (Å) and angles (°): Ti—O(1), 1.802(4); Ti—N(1), 2.193(5); Ti—S(1), 2.566(2); Ti—Cl(1), 2.287(2); Ti—Cl(2), 2.246(2); Ti—Cl(3), 2.324(2); O(1)—C(1), 1.331(6); C(1)—C(6), 1.395(7); C(6)—C(7), 1.428(7); C(7)—N(1), 1.295(6); N(1)—C(8), 1.449(7); C(8)—C(13), 1.388(8); C(13)—S(1), 1.769(6); S(1)—C(22), 1.824(7); O(1)—Ti—Cl(2), 104.9(1); N(1)—Ti—Cl(2), 170.8(1); Cl(1)—Ti—Cl(3), 164.3(1); O(1)—Ti—S(1), 162.5(1).

5c) have a high catalytic activity for ethylene–NBE copolymerization. Table 1 shows the ethylene–NBE copolymerization results by different catalysts at 1 atm of ethylene. Increasing in the steric hindrance of the alkyl units led to the decreasing in both catalytic activity and comonomer incorporation ratio (Table 1, entries 1–3). *n*-Alkylthio complexes **5a**,**d**–**f** all showed very high activities in the range 1.32–2.03 $\times$ 10^6 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1} (Table 1, entries 1, 4–6), which are much more active than phenylthio complex **5g** (0.23 $\times$ 10^6 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}) (Table 1, entry 7). The copolymerization behaviors of the catalysts and the structures of the copolymers were strongly influenced by the reaction conditions such as initial concentration of NBE, Al/Ti ratio, and copolymerization temperature, which was discussed in the previous communication in detail.[14]

Ethylene–Cyclopentene Copolymerization[18]

Complexes **5** have proven to be good catalysts for the copolymerization of ethylene with CPE at 1 atm of ethylene. The reaction conditions influenced strongly the copolymerization behaviors of the catalysts and the microstructures of the copolymers, which were shown in Table 2. The copolymerization activity was decreased and CPE incorporation ratio was increased with an increasing feed of CPE from 25 to 200 mmol (Table 2, entries 1–4). The glass transition temperature (T_g) of the resultant copolymer was increased with an increase of the CPE incorporation ratio, and was below -20 °C (Table 2, entries 1–4). When the copolymerization temperature was raised from 0 to 40 °C, the CPE incorporation ratio was increased and the molecular weight of copolymer was decreased (Table 2, entries 5, 6, and 2). As the Al/Ti ratio was varied from 250 to 2000, only slight variation of the activity and the CPE incorporation ratio was observed but molecular weight of copolymer was decreased (Table 2, entries 7–10). The possible reason for the decrease of M_w may be ascribed to the chain-transfer from the titanium to aluminum center.

The ethylene-CPE copolymerization results catalyzed by different catalysts were shown in Table 3. Complex **5c** with a bulky substituent had the lowest copolymerization activity and comonomer incorporation ratio (Table 3, entry 3). The catalytic activities of *n*-alkylthio complexes **5a**, **d**–**f** and comonomer incorporation ratio were in the range 1.60–2.32 $\times$ 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1} and 12.2–14.5 mol % (Table 3, entries 1, 4–6), respectively. These measured values are superior to those of the phenylthio complex **5g** (1.33 $\times$ 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1} and 9.6 mol % incorporation ratio, entry 7, Table 3).

To confirm the microstructure of our copolymers (Table 4), we synthesized the ethylene-CPE copolymer that was well characterized using V(acac)$_3$ as a catalyst according to the literature (Table 3, entry 8) for comparision.[18(g)] It was found that the ^{13}C NMR spectra of the ethylene-CPE copolymers produced by catalysts **5** were very similar to that of copolymer produced by V(acac)$_3$.[18(g)] As shown in Figure 2, the peaks at δ = 43.4 ppm and 43.9 ppm were assigned to the methine carbons (C_2) in the isolated CPE units and in the ethylene-*alt*-CPE units with CPE *cis*-1,2-enchained respectively, with m conformation. When the comonomer incorporation ratio was low [such as 5.5 mol %; Fig. 2(b)], the alternated triads CPE-E-CPE in copolymer decreased, in which one CPE unit was mostly separated by more than two ethylene units. The ethylene-*alt*-CPE fragment was increased with the

Table 1. Results of Copolymerization of Ethylene with Norbornene Catalyzed by Different Catalysts[a]

Entry	R	NBE (mmol)	Al/Ti	T_p (°C)	Yield (g)	Activity[b]	NBE Content[c]	M_w[d]	M_w/M_n[d]	T_g (°C)[e]
1	 (**5a**)	20	500	50	2.033	2.03	43.9	25.63	1.54	109.3
2	 (**5b**)	20	500	50	0.231	0.23	31.3	13.72	1.80	58.1
3	 (**5c**)	20	500	50	0.002	0.002	–	–	–	–
4	 (**5d**)	20	500	50	1.647	1.65	44.9	30.03	1.77	119.9
5	 (**5e**)	20	500	50	1.479	1.48	38.7	34.40	1.46	88.4
6	 (**5f**)	20	500	50	1.322	1.32	36.2	26.24	1.54	n.o.[f]
7	 (**5g**)	20	500	50	0.229	0.23	30.9	6.79	1.49	66.6

[a] Copolymerization conditions: ethylene, 0.1 MPa; toluene, 40 mL; V_{total}, 45.8 mL; catalyst, 4 mmol (3 μmol/mL in toluene); reaction time, 15 min; NBE (5.95 M in toluene).
[b] Activity: 10^6 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}.
[c] Determined by ^{13}C NMR spectroscopy, mol %.
[d] Determined by GPC relative to polystyrene standards, $\times 10^{-4}$ g mol^{-1}.
[e] Determined by DSC.
[f] n.o., not observed.

increasing of the comonomer incorporation ratio [Fig. 2(c)] and became the major component in the copolymer chain when the comonomer incorporation ratio reached 42.2 mol % [Fig. 2(d)].

Ethylene–Dicyclopentadiene Copolymerization[16,19]

The structure of DCPD contains a NBE and a CPE unit. Since both units are good comonomers for the aforementioned copolymerization, we wondered which C=C double bond would participate in the copolymerization reactions if DCPD were used as a monomer. In the presence of MMAO, complexes **5** proved to be effective catalysts for ethylene copolymerization with DCPD at 1 atm of ethylene. The copolymerization results were summarized in Table 5. The increasing feed of DCPD from 5 to 30 mmol at 1 atm of ethylene led to the decrease in copolymerization activity, but the increase in both DCPD incorporation ratios and the molecular weights (Table 5, entries 1–4). The glass transi-

Table 2. Results of Copolymerization of Ethylene with Cyclopentene Catalyzed by 5a/MMAO[a]

Entry	CPE (mmol)	Al/Ti	T_p (°C)	Yield (g)	Activity[b]	CPE Content[c]	M_w[d]	M_w/M_n[d]	T_g (°C)[e]	T_m (°C)[e]
1	25	1000	40	1.320	2.20	10.7	2.44	4.35	−35.0	104.8
2	50	1000	40	0.886	1.48	14.4	3.67	1.58	−31.7	110.0
3	150	1000	40	0.141	0.24	26.3	3.67	1.77	−25.8	n.o.[f]
4	200	1000	40	0.095	0.16	27.6	3.89	1.70	−23.5	n.o.
5	50	1000	0	1.021	1.70	7.4	24.60	2.19	n.o.	n.o.
6	50	1000	20	0.808	1.35	13.0	8.91	1.97	−29.4	112.5[g]
7[h]	50	250	40	0.651	1.09	9.6	6.58	1.77	n.o.	n.o.
8[h]	50	500	40	0.776	1.29	10.2	5.02	1.77	n.o.	n.o.
9[h]	50	1000	40	0.603	1.01	11.9	4.57	1.69	n.o.	109.5
10[h]	50	2000	40	0.712	1.19	11.0	3.80	1.68	n.o.	107.5

[a] Copolymerization condition: ethylene, 0.1 MPa; catalyst, 12 mmol (3 μmol/mL in toluene); 30 min; no additional solvent except for 4 mL of toluene for solving the precatalyst and 6.3 mL of MMAO toluene solution.
[b] Activity: 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}.
[c] Determined by ^{13}C NMR spectroscopy, mol %.
[d] Determined by GPC relative to polystyrene standards, $\times 10^{-4}$ g mol^{-1}.
[e] Determined by DSC.
[f] n.o., not observed.
[g] DSC scan: 40 °C/min.
[h] Solvent, toluene; V_{total}, 21 mL.

Table 3. Results of Copolymerization of Ethylene with Cyclopentene Catalyzed by Different Catalysts[a]

Entry	Cat.	R	Yield (g)	Activity[b]	CPE Content[c]	M_w[d]	M_w/M_n[d]	T_g (°C)[e]	T_m (°C)[e]
1	**5a**		1.093	1.46	11.2	4.10	2.07	n.o.[f]	n.o.[f]
2	**5b**		1.778	2.37	3.3	3.82	3.60	n.o.	111.3
3	**5c**		0.118	0.16	<1.0	5.50	2.08	n.o.	124.0
4	**5d**		1.666	2.22	12.4	2.10	2.56	−34.6	104.5
5	**5e**		1.673	2.23	13.4	2.04	2.93	−30.5	104.1
6	**5f**		1.741	2.32	14.5	2.06	2.88	−26.0	103.0
7	**5g**		1.000	1.33	9.6	2.85[g]	6.28[g]	−18.3	116.9
8	$V(acac)_3$[h]		0.072	0.00004	29.0	3.91[i]	11.64[i]	n.o.	–

[a] T_p, 40 °C; catalyst, 15 mmol (3 μmol/mL in toluene); reaction time, 30 min; cyclopentene, 50 mmol; Al/Ti, 500; tolune, V_{total} 25 mL.
[b] Activity: 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}.
[c] Determined by ^{13}C NMR spectroscopy, mol %.
[d] Determined by GPC relative to polystyrene standards, $\times 10^{-4}$ g mol^{-1}.
[e] Determined by DSC.
[f] n.o., not observed.
[g] Bimodal; main peak: $M_w = 1.05 \times 10^4$ g mol^{-1}, $M_w/M_n = 2.49$.
[h] Copolymerization condition: 10% of ethylene mixed with nitrogen; toluene, 20 mL; Et_2AlCl, 18 mmol; $V(acac)_3$, 3.6 mmol; cyclopentene, 150 mmol; T_p, 0 °C; reaction time, 5 h.
[i] Bimodal; main peak: $M_w = 3.34 \times 10^4$ g mol^{-1}, $M_w/M_n = 2.18$.

tion temperature (T_g) of the copolymer depended strongly on the content of DCPD. For example, T_g was increased from 5 to 53 °C (Table 5, entries 1–4) as DCPD incorporation ratios were changed from 11 to 20 mol %. This phenomenon was also observed in ethylene-CPE copolymers. Variation of the Al/Ti ratio from 250 to 2000 slightly influenced the catalysts activities and the DCPD incorporation ratio, but resulted in the decrease in the molecular weights of the copolymers (Table 5, entries 2, 5–7). When the copolymerization temperature was raised from 0 to 70 °C, the catalyst activity was first increased and then decreased (Table 5, entries 2, 8–10). The optimal reaction temperature was 50 °C at which the activity was up to 8.19×10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1} (entry 9, Table 5).

Table 6 showed the effects of catalysts on the ethylene-DCPD copolymerization. As shown in this table, the bulky alkyl substituents on sulfur resulted in a decrease in both catalytic activity and comonomer incorporation ratio (Table 6, entries 1–3). The methylthio complex **5a** exhibited the highest catalytic activity of 8.19×10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}, which was about eight times higher than the corresponding phenylthio complex **5g** (Table 6, entry 1 vs. 7). The activity of complexes **5d–f** fell in between 5.67 and 6.63×10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}, which is slightly lower than the methylthio complex **5a** (Table 6, entries 4-6 vs 1). The comonomer incorporation ratio of *n*-alkylthio complexes **5a**, **d–f** was comparable to phenylthio complex **5g** (Table 6;

Table 4. Ethylene–Cyclopentene Copolymerization Catalyzed by **5a**/MMAO Under Different Conditions[a]

Entry	**5a** (μmol)	CPE (mmol)	Al/Ti	T_p (°C)	t (h)	Yield (g)	Activity[b]	CPE Content[c]
1	12	25	1500	0	0.5	1.474	2.46	5.5
2	12	50	1000	40	0.5	0.886	1.48	14.4
3[d]	20	150	500	40	6	0.010	0.00083	42.2

[a] Copolymerization conditions: ethylene, 0.1 MPa; catalyst, 3 μmol/mL in toluene.
[b] Activity: 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}.
[c] Determined by ^{13}C NMR spectroscopy, mol %.
[d] 10% of ethylene mixed with nitrogen.

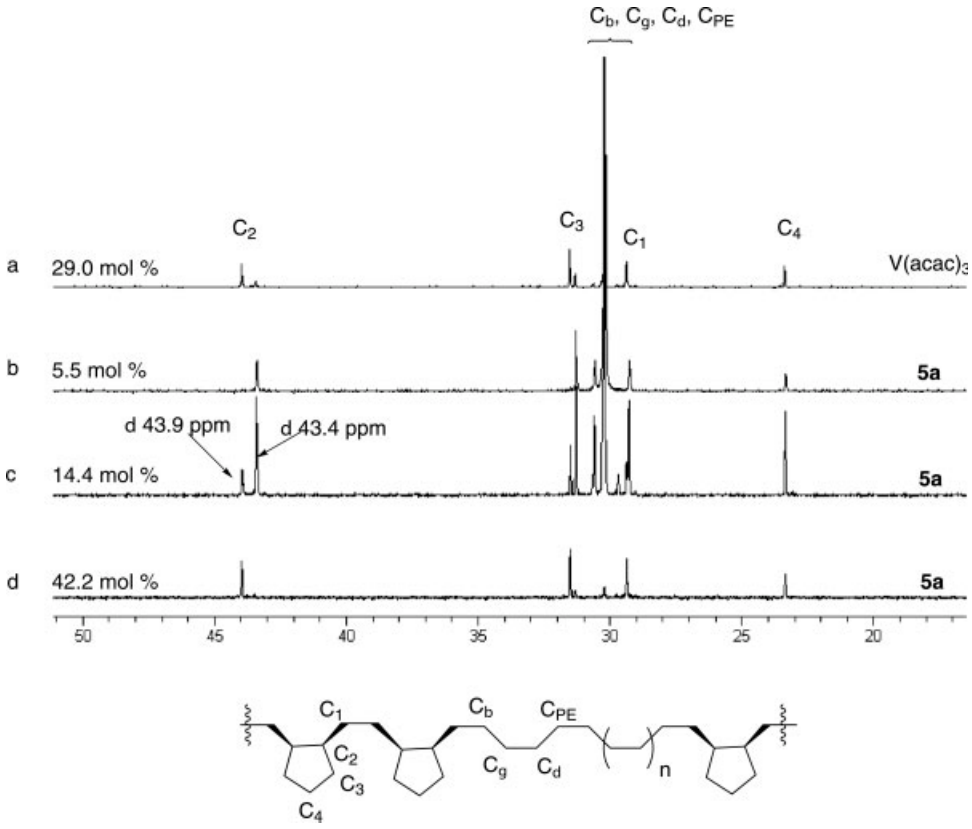


Figure 2. ^{13}C NMR spectra of the ethylene-CPE copolymers produced by catalysts **5a** and V(acac)3.

entries 1, 4–7). The molecular weight distributions of the copolymers generated by **5a–f** were below 1.6, similar to those produced by single-site catalysts.[20]

The ^{1}H and ^{13}C NMR analyses of the resultant copolymer indicated that the copolymerization might proceed through enchainment of the NBE ring.[19(c)] Further, functionalization of the

Table 5. Results of Ethylene-Dicyclopentadiene Copolymerization Catalyzed by **5a**/MMAO[a]

Entry	DCPD (mmol)	Al/Ti	T_p (°C)	Yield (g)	Activity[b]	DCPD Content[c]	M_w[d]	M_w/M_n[d]	T_g (°C)[e]
1	5	500	25	1.814	9.07	11.6	9.01	1.68	5.9
2	10	500	25	1.223	6.12	14.4	21.59	1.68	22.9
3	20	500	25	1.055	5.28	19.1	31.77	1.46	43.8
4	30	500	25	0.178	0.89	20.4	51.21	1.36	52.7
5	10	250	25	1.408	7.04	11.8	19.32	1.69	21.3
6	10	1000	25	1.417	7.09	14.1	17.84	1.84	16.5
7	10	2000	25	1.290	6.45	13.0	14.38	1.78	10.5
8	10	500	0	0.108	0.54	12.0	30.71	1.82	n.o.[f]
9	10	500	50	1.637	8.19	20.2	7.61	1.58	47.0
10	10	500	70	0.762	3.81	28.0	4.22	1.40	69.7

[a] Copolymerization condition: ethylene, 0.1 MPa; solvent, toluene; V_{total}, 30 mL; catalyst, 12 mmol (3 μmol/mL in toluene); reaction time, 10 min; DCPD, 3.94 M in toluene.
[b] Activity: 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}.
[c] Determined by ^{1}H NMR spectroscopy, mol %.
[d] Determined by GPC relative to polystyrene standards, $\times 10^{-4}$ g mol^{-1}.
[e] Determined by DSC.
[f] n.o., not observed. T_m = 85.2 °C.

Table 6. Results of Ethylene-Dicyclopentadiene Copolymerization Catalyzed by Different Catalysts[a]

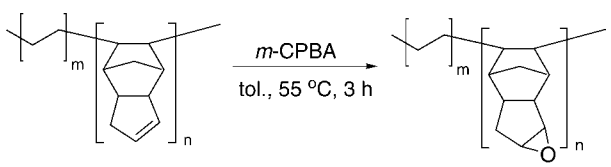
Entry	Cat.	R	Yield (g)	Activity[b]	DCPD Content[c]	M_w[d]	M_w/M_n[d]	T_g (°C)[e]
1	**5a**		1.637	8.19	20.2	7.61	1.58	47.0
2	**5b**		0.359	1.80	17.1	8.70	1.33	29.1
3	**5c**		0.007	0.035	15.7	–	–	–
4	**5d**		1.326	6.63	23.0	7.24	1.33	63.1
5	**5e**		1.134	5.67	19.7	7.17	1.56	50.8
6	**5f**		1.247	6.24	20.7	7.38	1.12	49.7
7	**5g**		0.197	0.99	20.0	12.14	3.07	53.8[f]

[a] Copolymerization conditions: ethylene, 0.1 MPa; toluene, 20.3 mL; V_{total}, 30 mL; Al/Ti, 500; T_p, 50 °C; catalyst, 12 mmol (3 μmol/mL in toluene); reaction time, 10 min; DCPD, 10 mmol (3.94 M in toluene).
[b] Activity: 10^5 g Polymer (mol Ti)$^{-1}$ h^{-1} atm^{-1}.
[c] Determined by ^{1}H NMR spectroscopy, mol %.
[d] Determined by GPC relative to polystyrene standards, $\times 10^{-4}$ g mol^{-1}.
[e] Determined by DSC.
[f] T_m = 117.0 °C.

remaining C=C double bonds in the resulting copolymers would provide a possible way to generate new functionalized copolymers with improved properties. It was found that the olefinic groups of the ethylene-DCPD copolymer could be quantitatively converted to the epoxy groups using *m*-chloroperbenzoic acid (*m*-CPBA) as an oxidant (Scheme 2, for manipulation see experimental part, for NMR see Supporting Information).[19(c)]

CONCLUSIONS

A family of [O$^-$NS^R]TiCl$_3$ complexes containing phenoxyimine ligands with appended alkylthio groups was synthesized and fully characterized. Upon activation by MMAO, these complexes (except for **5c**) were all very effective catalysts for ethylene copolymerization with cycloolefins such as NBE, CPE, and DCPD. The reaction conditions and the steric hindrance of the alkyl substituents on sulfur atom in the precatalysts proved to influence strongly the copolymerization behaviors of the catalysts and the microstructures of the copolymers. Increasing in the steric hindrance of the alkylthio units led to a decrease in comonomer incorporation ratios. Compared with complex **5g**, *n*-alkylthio complexes **5a**,**d–f** all exhibited better ethylene–cycloolefins copolymerization capabilities. Those bearing linear alkyl groups (**5d–f**) showed a similar activity, which was almost independent of the chain length. Nevertheless, the longer alkyl chains largely enhanced the thermal stability of the resultant catalysts. The glass transition temperatures of the copolymers were increased as the comonomer incorporation ratios increased.



Scheme 2

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