Electron Spin Resonance Spectroscopy Study on Reduction of Constrained-Geometry Catalyst Systems

Zhibin Ye, Wen-Jun Wang, Shiping Zhu

Department of Chemical Engineering, McMaster University, 1280 Main Street West, Hamilton, Ontario, L8S 4L7 Canada

Received 12 September 2002; accepted 22 November 2002

ABSTRACT: The reduction of a constrained-geometry catalyst ($CGCTiMe_2$) activated with a series of cocatalysts, including modified methylaluminoxane (MMAO), tris(pentafluorophenyl) borane [$B(C_6F_5)_3$], and combined $B(C_6F_5)_3$/MMAO, was experimentally investigated using an on-line electron spin resonance spectroscopy (ESR) technique. The effects of the solvent type, cocatalyst/catalyst ratio, and temperature on the reduction were examined. In the $CGCTiMe_2$/MMAO system, increasing the Al/Ti molar ratio from 20 to 250 significantly increased the Ti(III) content. Adding trimethylaluminum to the system lowered the Ti(III) content. Three trivalent Ti species, **Ti(a)** (g = 1.972), **Ti(b)** [g = 1.992, α(H) = 7.4 G], and **Ti(c)** (g = 1.995), were observed. In the $CGCMe_2/B(C_6F_5)_3$ system, only one trivalent Ti species (g = 1.988) was observed. The $CGCTiMe_2/B(C_6F_5)_3$ system was more stable to reduction than the $CGCTiMe_2$/MMAO system. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 2474–2482, 2003

Key words: electron paramagnetic resonance; metallocene catalysts; organometallic catalysts; polyolefins; transition metal chemistry

INTRODUCTION

Metallocene-based coordination catalysts have a significant impact on polyolefin industries.[1] An important development in technology is the constrained-geometry catalyst (CGC)[2–8] [($Cp^*SiR_2NR)MX_2$, where Cp* = tetramethylcyclopentadienyl, R = alkyl, M = Group 3 or 4 transition metal, and X = CH_3 or Cl (e.g., **Scheme 1**)]. The CGC system, among the first commercialized single-site catalysts,[9] is able to produce a new family of polyethylene with long-chain branching.[10–12] This exceptional characteristic provides polymers with the combination of good processibility and desirable strength properties. Meanwhile, the CGC system is remarkably stable even at high polymerization temperatures (>140°C). Moreover, it was reported that the reduction of titanium CGCs by methylaluminoxane (MAO) was less significant than that of other titanocenes.[13]

The study of catalyst reduction is very important for elucidating the active site structure and for understanding the reaction mechanism and kinetics in catalyst polymerization. In this regard, the electron spin resonance (ESR) technique appears to be a useful tool for investigating catalyst reduction in the polymerization of olefin[14–17] and that of syndiotactic styrene.[18–23] On-line monitoring of the paramagnetic trivalent Ti(III) or Zr(III) signals provides both qualitative and quantitative information about the reduction mechanism and kinetics. In olefin polymerization, some studies showed that tetravalent cationic metallocene complexes are the active sites for olefin monomers and are reduced to inactive paramagnetic trivalent complexes during polymerization.[14–17] The reduction is believed to be attributable to a reductive decomposition of an electron-deficient bridging complex of catalyst and cocatalyst by ejecting nonbridged alkyl groups.[14,15] In an early study on a homogeneous Cp_2TiCl_2/AlR_xCl_{3-x} system, Olivé et al.[14] proposed that reduction was from a bimolecular second-order mutual deactivation of two Ti(IV) active sites. However, the attribution of active sites in half-sandwich metallocene catalysts for syndiotactic styrene polymerization remains a controversy. It used to be believed that reduced trivalent cationic complexes were the active sites based on the correlations between polymerization kinetic data and ESR analysis,[18–22] although other studies observed no or very weak ESR signals attributed to trivalent complexes, showing no correlation with the polymerization data.[23]

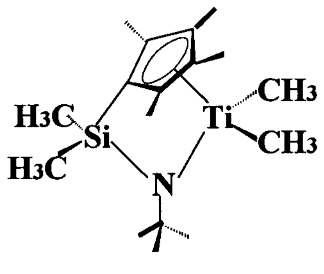
As an important catalyst system, CGC has attracted considerable investigative efforts. However, to the best of our knowledge, a systematic reduction study on this catalyst system has not been reported. In this work we used an on-line ESR technique to investigate experimentally the reduction of the $CGCTiMe_2$ catalyst activated with different cocatalyst systems, including modified MAO (MMAO), tris(pentafluoro-

---

Correspondence to: S. Zhu (zhuship@mcmaster.ca).

Contract grant sponsor: Natural Sciences and Engineering Research Council of Canada (NSERC).

Journal of Applied Polymer Science, Vol. 89, 2474–2482 (2003)



1

Scheme 1

phenyl) borane [$B(C_6F_5)_3$], and combined MMAO/$B(C_6F_5)_3$ cocatalyst systems.

EXPERIMENTAL

Materials and preparations

CGC catalyst precursor {[$C_5Me_4(SiMe_2N^tBu)$]$TiMe_2$ (Me: methyl, ^{t}Bu: isobutyl, C_5: cyclopentadiene)} and borane cocatalyst [$B(C_6F_5)_3$] were provided by Dow Chemical (Midland, MI) and Boulder Scientific, respectively. Modified methylaluminoxane (MMAO-3A with 65.9% methane and 31.7% isobutene; Akzo-Nobel Corp.) as 6.68 wt % aluminum in heptane and 11.6% in toluene was used as the MAO source in the experiments. Trimethylaluminum (TMA) was provided by Aldrich Chemical (Milwaukee, WI) as 2 mol/L solution in toluene. The catalysts and cocatalysts were used as received. Anhydrous-grade toluene and heptane supplied by Aldrich Chemical were refluxed over sodium with benzophenone as indicator for 48 h and distilled out before use. All manipulations of catalyst and cocatalyst solutions and ESR samples were conducted in a controlled nitrogen drybox or under nitrogen protection.

ESR sample preparation and analysis

Screw-capped ESR sample tubes were used in this work. The samples were prepared as follows. In a drybox, a proper amount of solvent was injected into the ESR tube by syringe. A prescribed amount of cocatalyst solution [MMAO or $B(C_6F_5)_3$] was then added to the tube. For the mixed cocatalyst systems [MMAO/TMA, MMAO/$B(C_6F_5)_3$], MMAO solution was added first, followed by the addition of a certain amount of TMA or $B(C_6F_5)_3$ solution by syringe. The ESR tube was then capped and wrapped with Parafilm. The sample was then transferred to an Aldrich AtmosBag filled with UHP nitrogen. A desired amount of the catalyst precursor solution was finally added before ESR measurement.

The ESR measurements were conducted at different temperatures using a Bruker EP072 X-band ESR spectrometer (Bruker Instruments, Billerica, MA) equipped with a temperature-control unit. Spin concentration calibrations at different temperatures were carried out by use of standard TEMPO solutions (10^{-5}–10^{-3} molar) for quantitatively determining the Ti(III) concentration. The magnetic field was calibrated with DPPH. The ESR measurement conditions were as follows: magnetic modulation frequency 100 kHz, intensity 20 dB, central magnetic field 3400 G, swift range 600 G, receive gain 2×10^{-4}, and modulation amplitude 5 G. Bruker WinEPR SimFonia (version 1.25) software was used to simulate the experimental spectrum.

RESULTS AND DISCUSSION

MMAO as cocatalyst

MAO is one of the most commonly used cocatalysts for metallocene polymerization of olefin monomers. However, conventional MAO has a low solubility in aliphatic solvents as well as poor storage stability in solution. Modified MAO (MMAO) prepared by controlled hydrolysis of TMA and TiBA has greater solubility and better storage stability in solvent than that of MAO for olefin polymerization.[1(f)] In this work MMAO was used as MAO source.

The Ti(IV) reduction in the $CGCTiMe_2$/MMAO system with different Al/Ti ratios was carried out in toluene at various temperatures. Figure 1(a) shows a set of experimental ESR spectra at different aging times and 100°C with an original $CGCTiMe_2$ concentration of 5×10^{-4} mol/L and Al/Ti molar ratio of 100. The ESR spectra collected after 2-min reaction with Al/Ti molar ratios ranging from 20 to 2000 are presented in Figure 2. Three Ti(III) paramagnetic signals can be resolved by a computer simulation: two singlets, **Ti(a)** ($g = 1.972$) and **Ti(c)** ($g = 1.995$); and one doublet, **Ti(b)** [$g = 1.992$, $\alpha(H) = 7.4$ G]. The simulated signals and their combined resulting spectra with relative intensities of the three individual signals are also included in Figure 1(b) and (c), respectively. The singlet **Ti(c)** and doublet **Ti(b)** overlap each other. There are some satellite lines in **Ti(b)** attributed to the $\alpha(Ti) = 8.2$ G hyperfine interaction with ^{47}Ti (7.28% abundance, $I = 5/2$) and ^{49}Ti (5.51% abundance, $I = 7/2$). These lines, although weak because of signal overlap, are observable in Figure 1. The integral intensity of the satellite lines constituted about 12.8% of the total area, corresponding to the natural abundance of ^{47}Ti and ^{49}Ti. No resolvable hyperfine splitting was found with **Ti(a)** and **Ti(c)** signals.

The intensities of the three paramagnetic signals varied with the aging time. At the beginning of aging, only **Ti(a)** and **Ti(b)** were observed (see Fig. 1). The intensity of **Ti(b)** then increased and that of **Ti(a)** decreased gradually. In about 2 min a new signal,

Ti(c), appeared. The **Ti(c)** signal gained its intensity quickly and gradually overlaid the **Ti(b)** signal. In 30 min the **Ti(a)** signal disappeared and **Ti(b)** was overwhelmed by **Ti(c)**. Applying a further derivative to the shown spectra gave evidence for the existence of **Ti(b)** through aging time. The intensities of the three Ti(III) signals also changed with the Al/Ti molar ratio. The **Ti(a)** signal was present in the initial period of reaction with the Al/Ti molar ratios lower than 250. At high Al/Ti molar ratios (>250), only **Ti(b)** and **Ti(c)** were observable. The variation of the relative intensities of these signals with the Al/Ti molar ratio in Figure 2 followed the same pattern as that with the aging time in Figure 1(a). Similar changes in spectra with time and Al/Ti ratio were also observed in a half-sandwich metallocene trichloride/MAO system by Chien et al.[15]

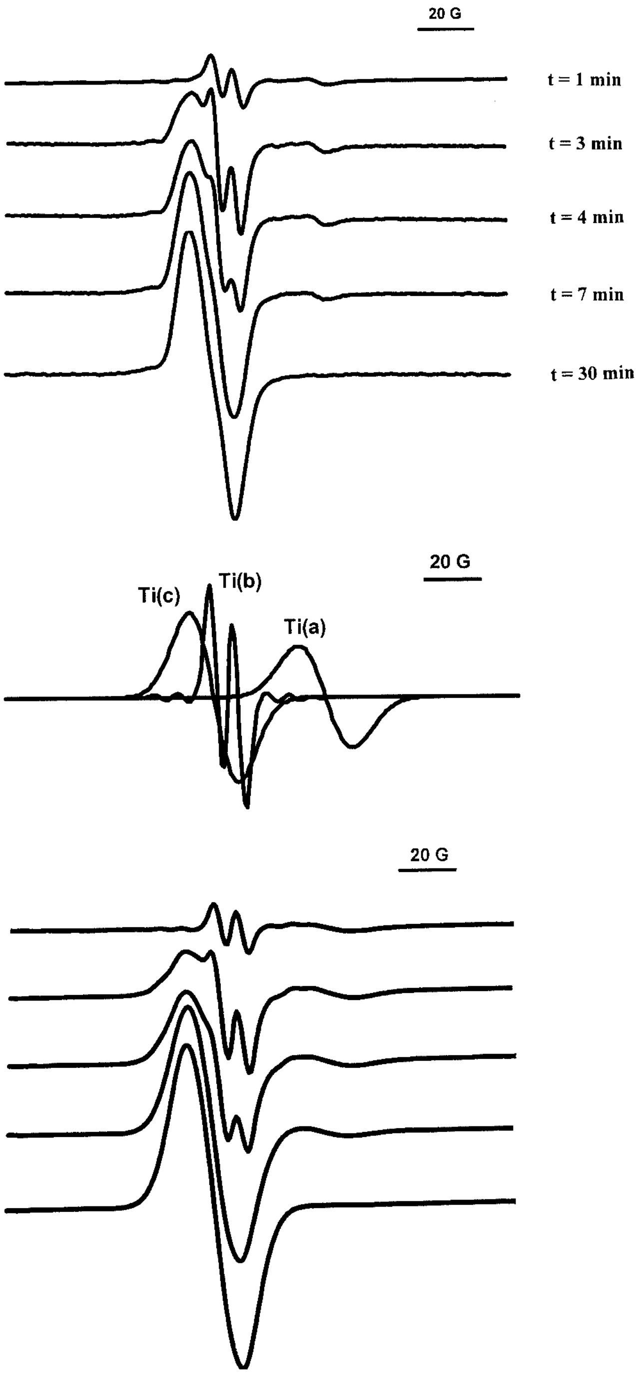


Figure 1 (a) ESR spectra (from 3300 to 3480 G) recorded at different times during the reduction of the CGCTiMe$_2$/MMAO system in toluene with $[Ti]_0 = 5 \times 10^{-4}$ *M*, Al/Ti = 100 (molar), and T = 100°C. (b) The computer-simulated Ti(a), Ti(b), and Ti(c) signals. (c) Computer-simulated spectra parallel to (a).

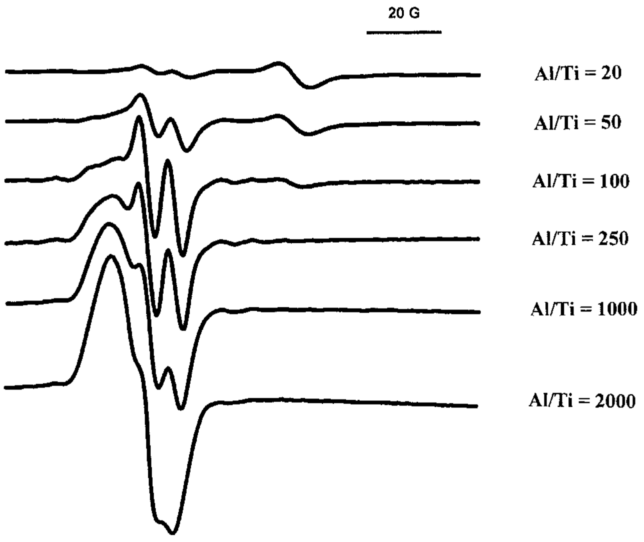
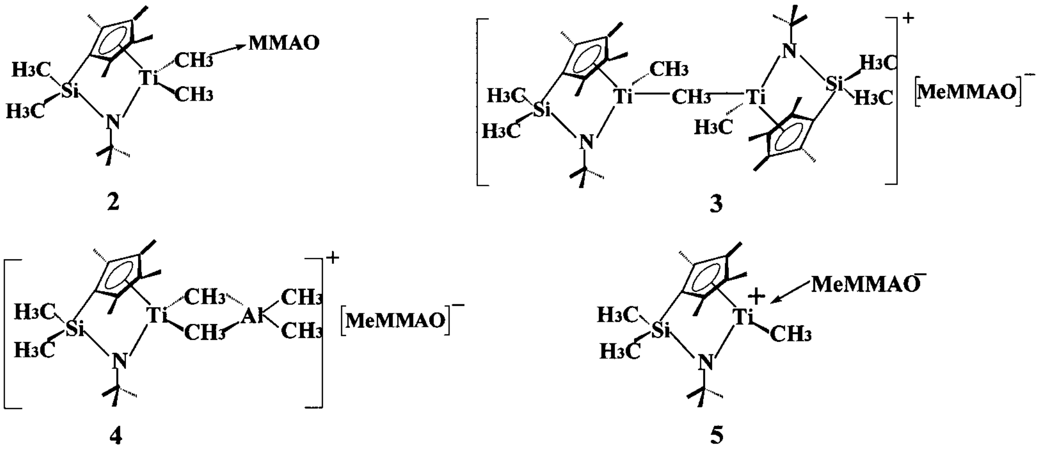


Figure 2 ESR spectra (from 3340 to 3460 G) recorded at T = 100°C for the CGCTiMe$_2$/MMAO system in toluene with $[Ti]_0 = 5 \times 10^{-4}$ *M* and different Al/Ti molar ratios.

In the CGCTiMe$_2$/MMAO system, there could be four CGCTiMe$_2$/MMAO complexes, as shown in **Scheme 2**: weak complex of CGCTiMe$_2$ with MMAO (**2**), binuclear cationic ion pair (**3** and **4**), and monomeric cationic ion pair (**5**). The existence of these four species is dependent on the Al/Ti ratio. These species have been elucidated by detailed ^{13}C- and ^{1}H-NMR studies on dialkyl metallocence/MAO systems.[24] Because binuclear cationic ion pairs **3** and **4** are quite stable, the reduction is mainly attributed to the elimination of the nonbridged methyl group from complexes **2** and **5**. The NMR studies showed that weak complexes of metallocene/MAO were present only at low Al/Ti ratios.[24] Note that **Ti(a)** was also present only at low Al/Ti ratios. **Ti(a)** is therefore believed to be a reduction product from the weak complex of CGCTiMe$_2$ with MMAO (**2**). In the CpTiCl$_3$/MAO system reported by Chien et al.[15] a similar assignment was proposed for the trivalent Ti species formed at low Al/Ti ratio. The NMR studies on metallocene dialkyl/MAO systems also showed that the concentration of the monomeric ion pair increased with the Al/Ti ratio and that it was the major complex at high Al/Ti ratios. In this work **Ti(c)** was the dominant

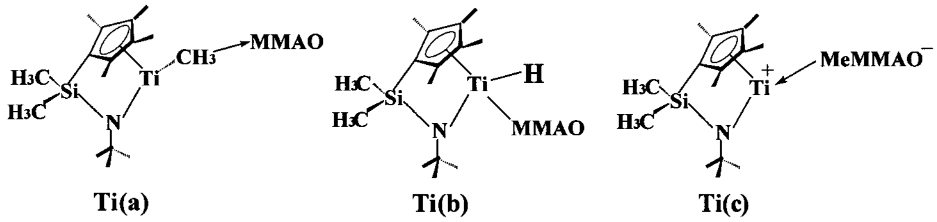


Scheme 2

signal in the ESR spectra and its intensity increased with the time and Al/Ti ratio. This parallelism leads us to assign **Ti(c)** as a reduction product from the monomeric cationic ion (**5**). The structures of **Ti(a)** and **Ti(c)** are proposed in **Scheme 3**. **Ti(b)** is a trivalent titanium hydride with g = 1.992, α(H) = 7.4 G, and α(Ti) = 8.2 G. The g and α(H) values of this species are very similar to those of the previously reported trivalent Ti hydrides in the $CpTiCl_3$/MAO system [g = 1.989, α(H) = 7.4 G; g = 1.995, α(H) = 4.5 G],[15] the $CpTi(OBu)_3$/MAO system [g = 1.989, α(H) = 7.0 G],[19] the $Cp^*TiMe_3/B(C_6F_5)_3$ system [g = 1.994, α(H) = 8.4 G],[23(d)]) and the SiO_2-supported $CpTiCl_3$/MAO system [g = 1.989, α(H) ≅ 7.4 G].[21(a)]) Its α(Ti) value is also very similar to that of the reported Ti(III) hydrides in $CpTiCl_3$/MAO [α(Ti) = 8 G][15] and $CpTi(OBu)_3$/MAO [α(Ti) ≅ 7 G] systems.[19] These similarities suggest the assignment of titanium hydride. This **Ti(b)** species, shown in **Scheme 3**, is probably a further reaction product of **Ti(a)**. Titanium hydrides with similar structures were also proposed in the $CpTiCl_3$/MAO and $CpZrCl_3$/MAO systems.[15]

The effects of the Al/Ti molar ratio on the reduction of the $CGCTiMe_2$/MMAO/toluene system are shown in Figures 3 and 4. The reduction occurred with a relatively high initial rate, but slowed down quickly with the Ti(III) concentration being leveled off after about 5 min of reaction. Increasing the Al/Ti molar ratio increased the reduction rate as well as the final Ti(III) concentration, particularly in the ratio range of 20–250, as shown in Figure 4. This is probably attributable to the increasing concentrations of **5** with the increase of Al/Ti ratios. However, further increases of the Al/Ti ratio from 250 had little effect on the reduction behavior.

MAO is an efficient cocatalyst for metallocene polymerization. It is prepared by a controlled hydrolysis of TMA with hydrated metal salts. Studies showed that free and associate TMA exist in the MAO solution. Polymerization studies were also conducted to examine the roles of TMA in catalysis.[25] In this work the effect of TMA on the $CGCTiMe_2$/MMAO reduction was conducted. A series of catalyst toluene solutions with $[Ti]_0 = 5 \times 10^{-4}$ *M*, Al(MMAO)/Ti = 500 (molar), and different [TMA]/[MMAO] ratios were prepared and investigated at 100°C. The ESR spectra showed the same three signals as those in the $CGCTiMe_2$/MMAO/toluene system. The changes of Ti(III) concentration with time are presented in Figure 5. Increasing the [TMA]/[MMAO] ratio decreased the Ti(III) concentration. This can be attributed to the coordination of TMA with the monomeric cationic ion pair (**5**) to form the methyl-bridged binuclear complexes $[CGCTi(\mu\text{-}Me)_2AlMe_2]^+[MeMMAO]^-$ (**4**), which is stable toward reduction and inactive for polymerization. The higher the [TMA]/[MMAO] ratio,



Scheme 3

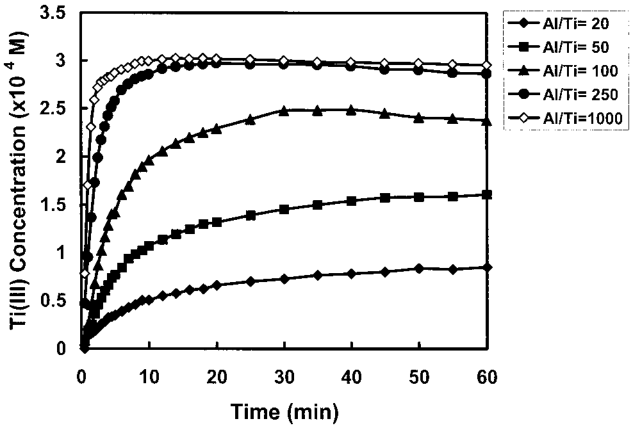


Figure 3 Ti(III) concentration versus time for the CGC-$TiMe_2$/MMAO system with different Al/Ti molar ratios at $[Ti]_0 = 5 \times 10^{-4}$ *M* and $T = 100°C$ in toluene.

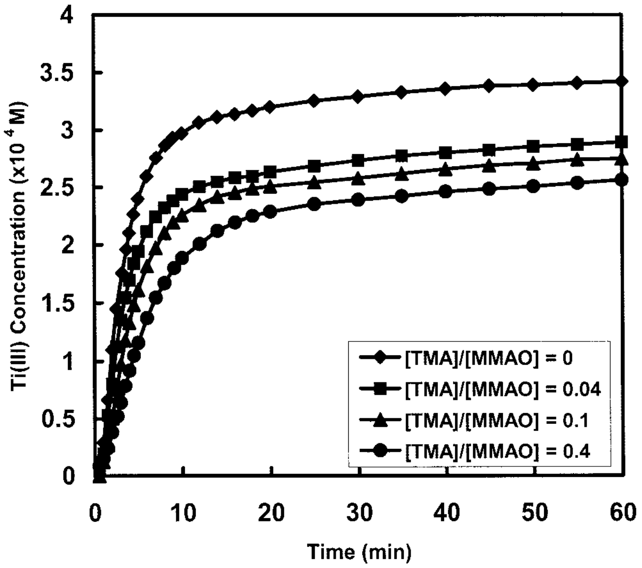


Figure 5 Ti(III) concentration versus time for the CGC-$TiMe_2$/MMAO/TMA system in toluene with different [TMA]/[MMAO] (molar Al) ratios at $[Ti]_0 = 5 \times 10^{-4}$ *M*, Al(MMAO)/Ti = 500 (molar), and $T = 100°C$.

the more **5** species were converted into **4**, and the lower the Ti(III) concentration. This result may have implications of lower activities with TMA addition in metallocene/MMAO systems.

The solvent effect on the $CGCTiMe_2$/MMAO reduction, by use of toluene and heptane, was also investigated. Figure 6 shows the ESR spectra for the CGC-$TiMe_2$/MMAO/heptane system. Different from the $CGCTiMe_2$/MMAO/toluene system, the spectrum shows a three-line overlapping signal. However, similar to the $CGCTiMe_2$/MMAO/toluene system, the spectrum changed with the aging time and Al/Ti molar ratio. Figure 7 shows the change of Ti(III) concentration with time in both heptane and toluene solutions. About 60% of the original Ti(IV) was reduced to Ti(III) in toluene in 10 min. However, in heptane only 10% original Ti(IV) was reduced to Ti(III).

One possible explanation of this phenomenon is the solvent coordination effect on the reduction of Ti(IV) complexes. Solvent coordination with cationic metallocene species is an important interaction for such complexes as $[Cp^*ZrMe_2]^+[MeB(C_6F_5)_3]^-$. The complex acts as a toluene adduct both in solution and in the solid state.[26] The coordination effect of arene with the constrained-geometry Zr cation $[CGCZrMe]^+$ was observed from both analytical and spectroscopic evidences.[27] Toluene is a coordinating solvent and heptane is a noncoordinating solvent. In our system, when toluene coordinates with the Ti(IV) complexes, it destabilizes the titanium–methyl bond in complexes **2** and **5**, leading to an easier breakup of the titanium–methyl bond and thus generate more Ti(III) species. Moreover, solvent coordination will also change the

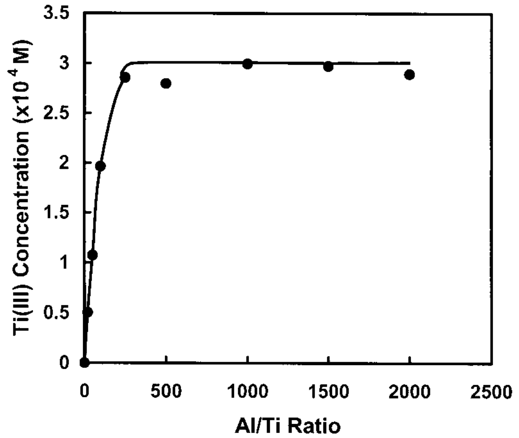


Figure 4 Ti(III) concentration versus Al/Ti molar ratio for the $CGCTiMe_2$/MMAO system with $[Ti]_0 = 5 \times 10^{-4}$ *M*, *t* = 10 min, and $T = 100°C$ in toluene.

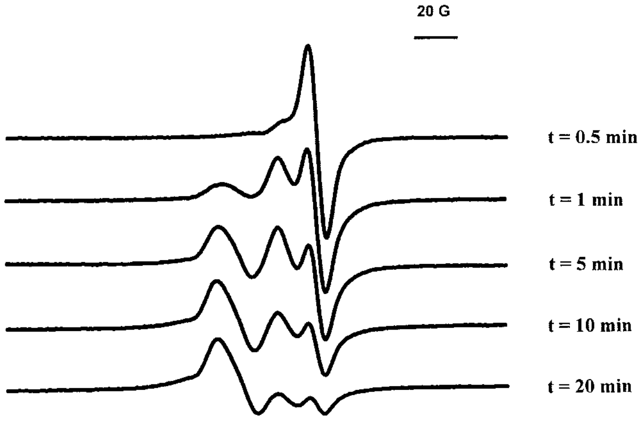


Figure 6 ESR spectra (from 3270 to 3500 G) recorded after different aging times for the $CGCTiMe_2$/MMAO system in heptane with $[Ti]_0 = 5 \times 10^{-4}$ *M*, Al/Ti = 300 (molar), and $T = 100°C$.

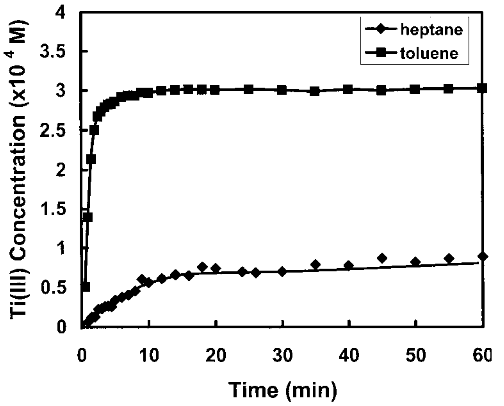


Figure 7 Ti(III) concentration versus time for the CGCTiMe$_2$/MMAO system in different types of solvent with $[Ti]_0 = 5 \times 10^{-4}$ *M*, Al/Ti = 1500 (molar), and T = 80°C.

unpaired spin density around the Ti(III) nucleus and cause the change of ESR signal.

Figure 8 shows the effect of temperature on the CGCTiMe$_2$/MMAO/toluene reduction with an original CGCTiMe$_2$ concentration of 5×10^{-4} *M* and [Al]/[Ti] molar ratio of 500. High temperature accelerated the reduction.

$B(C_6F_5)_3$ as cocatalysts

Different from MAO type of cocatalysts, perfluoroaryl boranes and borates react with metallocene compounds and yield an isolable and characterizable catalyst system.[1(f)] Many studies on this isolated complex have been carried out to elucidate this highly efficient catalytic system, especially for ethylene and α-olefin copolymerizations.[28]

The reaction of CGCTiMe$_2$ with $B(C_6F_5)_3$ generates the monomeric cationic species $[CGCTiMe]^+[MeB(C_6F_5)_3]^-$ (**6** in **Scheme 4**). Studies also showed that with a 2 : 1 ratio of CGCTiMe$_2$/$B(C_6F_5)_3$ in toluene, the dinuclear species $[CGCTiMe(\mu\text{-Me})MeTiCGC]^+$ $[MeB(C_6F_5)_3]^-$ (**7** in **Scheme 4**), in equilibrium with the monomeric species, was also generated.[28]

The ESR spectrum for equimolar CGCTiMe$_2$ and $B(C_6F_5)_3$ with $[Ti]_0 = 2 \times 10^{-2}$ *M* in toluene after 20 min at 100°C exhibited a singlet **Ti(d)** centered at g = 1.988, as shown in Figure 9. There were also some additional resonances at the shoulders of the singlet. These additional signals, also observed in the 2×10^{-2} *M* CGCTiMe$_2$/toluene without $B(C_6F_5)_3$, were probably attributable to Ti(III) alkoxides and/or other products arising from oxygen traces and impurities in the ESR tube at this high initial titanium concentration. The singlet is attributed to the Ti(III) species produced by the reductive methyl group elimination from the monomeric cationic species **6**. Its structure is proposed in **Scheme 5**. The intensity of this signal increased with the reduction time (Fig. 10).

For comparisons, a parallel ESR experiment under the same conditions but at 2 : 1 CGCTiMe$_2$ and $B(C_6F_5)_3$ molar ratio showed no Ti(III) species produced even after 1 h of reaction, except for the shoulder signals from impurities. It is known that at this B/Ti ratio, there is a large amount of species **7**. This result indicated that the dinuclear species are quite stable toward reduction.

Figure 10 shows the Ti(III) concentration as a function of reduction time for the CGCTiMe$_2$/$B(C_6F_5)_3$/toluene system at 100°C with different B/Ti molar ratios. It can be seen that after a 1-h reaction only about 1% of Ti(IV) was reduced to Ti(III) at B/Ti = 1, compared to the 60% for the CGCTiMe$_2$/MMAO at Al/Ti = 500 and the same temperature. Moreover, the reduction rates were much slower than that of the CGCTiMe$_2$/MMAO/toluene system. These results indicated that the monomeric cationic center **6** is much more stable than that of **5**. Increasing the B/Ti molar ratio increased the Ti(III) concentration because of the higher concentrations of **6** at the higher B/Ti ratios.

To investigate the temperature effect on the reduction, a series of samples with $[Ti]_0 = 2 \times 10^{-2}$ *M* and B/Ti = 1 (molar) at temperatures 40, 60, 80, and 100°C were analyzed. Unlike the CGCTiMe$_2$/MMAO system, no detectable signal was observed when the reaction temperature was lower than 80°C.

The solvent coordination also affected the reduction of the CGCTiMe$_2$/$B(C_6F_5)_3$ system. Two samples with $[Ti]_0 = 2 \times 10^{-2}$ *M* and B/Ti ratio = 1.0 (molar), but in different solvents (toluene and heptane), were prepared and investigated at 80°C. For the sample with heptane, no paramagnetic signal, except for those from impurities, was observed even after 1 h of reaction. However, for the sample in toluene, the **Ti(d)**

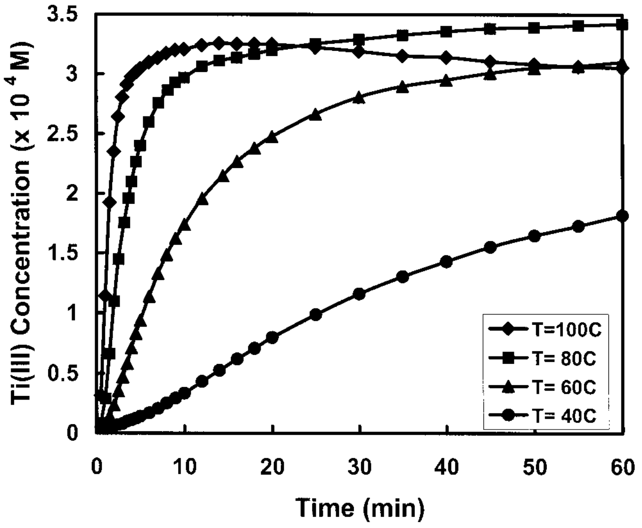
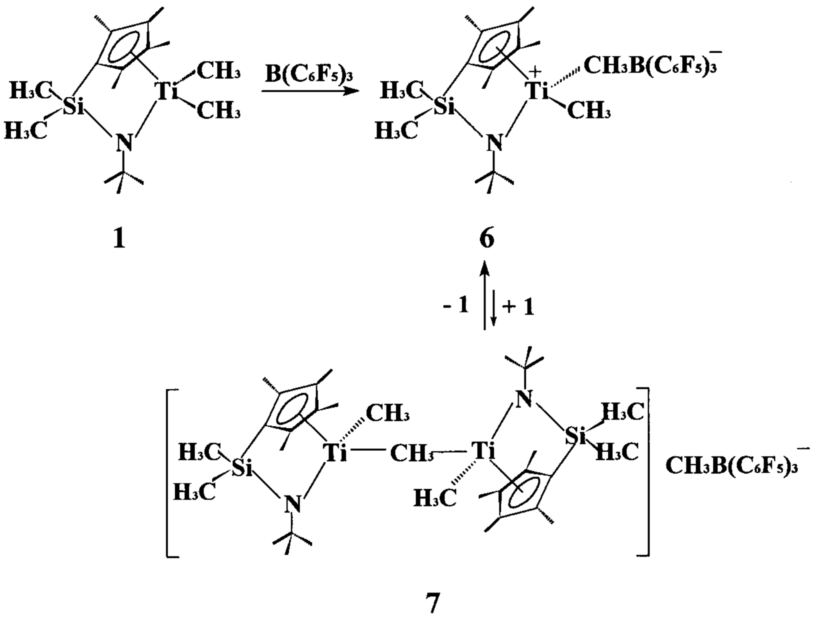


Figure 8 Ti(III) concentration versus time for the CGCTiMe$_2$/MMAO system at different temperatures with $[Ti]_0 = 5 \times 10^{[\text{minujs}]4}$ *M* and Al/Ti = 500 (molar) in toluene.



Scheme 4

signal was detected after 5 min and its intensity increased with the aging time.

B(C_6F_5)$_3$/MMAO as combined cocatalyst system

The CGCTiMe$_2$/B(C_6F_5)$_3$ system is very active for olefin polymerization. However, its high sensitivity toward trace impurities usually requires an addition of aluminum alkyls or MAO in polymerization. In this study the reduction of CGCTiMe$_2$ with the combined cocatalyst system B(C_6F_5)$_3$/MMAO was also studied.

The ESR spectra of the Ti(III) species in this mixed cocatalyst system were the same as those in the CGCTiMe$_2$/MMAO/toluene system. Figure 11 shows the effect of B/Ti molar ratio on the reduction with $[Ti]_0 = 5 \times 10^{-4}$ *M* and Al/Ti = 20 (molar). Compared to the CGCTiMe$_2$/MMAO system (B/Ti = 0 in Fig. 11), the Ti(III) concentrations were lower. Increasing the B/Ti molar ratio led to a lower Ti(III) concentration. This is attributed to the formation of the monomeric cationic ion pair $[CGCTiMe]^+[MeB(C_6F_5)_3]^-$ (**6**), which is more stable than **2** and **5** toward reduction.

A final point worth mentioning is that the activity of metallocene-type catalysts in olefin polymerization is well known to increase with the cocatalyst/catalyst ratio followed by a leveling off. However, in this investigation, it was shown that the concentration of the inactive Ti(III) species also increases with the Al/Ti or B/Ti ratio. This apparent contradiction is caused by a confusion of the activation/deactivation process. MAO or B(C_6F_5)$_3$ as a cocatalyst is required to activate the catalyst CGCTiMe$_2$ (i.e., to generate the active species **5** or **6**). A higher Al/Ti or B/Ti ratio yields a higher active site concentration and thus a higher polymerization rate. Viewed from another perspective, a higher active site concentration also induces a

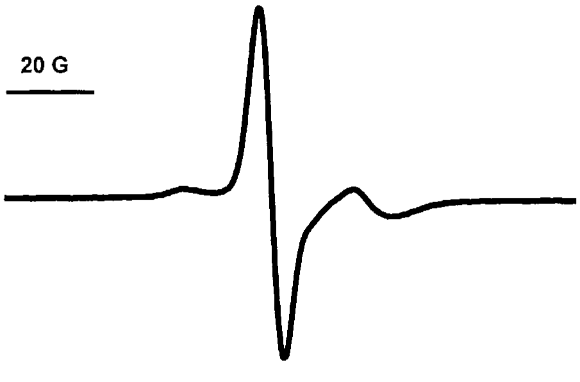
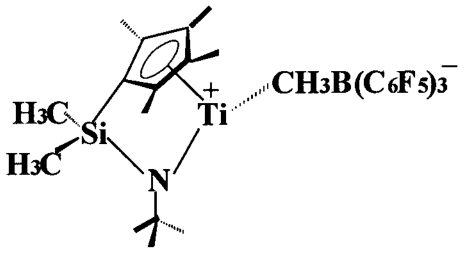


Figure 9 ESR spectrum for the CGCTiMe$_2$/B(C_6F_5)$_3$ system in toluene recorded at $[Ti]_0 = 2 \times 10^{-2}$ *M*, B/Ti = 1.0 (molar), *t* = 20 min, and *T* = 100°C.



Ti(d)

Scheme 5

higher reduction (deactivation) rate, giving a higher Ti(III) concentration.

CONCLUSIONS

In this work the reduction of $CGCTiMe_2$ activated with three different cocatalyst systems [MMAO, $B(C_6F_5)_3$, and combined $B(C_6F_5)_3$/MMAO] was investigated by use of an on-line ESR technique. In the $CGCMe_2$/MMAO system, three trivalent titanium species were generated from the reductive elimination of the methyl group in the $CGCTiMe_2$/MMAO weak complex (**2**) and in the monomeric cationic pair (**5**). The solvent coordination of toluene made Ti(IV) complex more amenable to reduction. The Ti(III) concentration increased with the Al/Ti molar ratio from 20 to 250 and leveled off after Al/Ti = 250. The reduction rate increased with temperature and Al/Ti molar ratio. Adding TMA to the system lowered the Ti(III) concentration as a result of the production of stable heterogeneous dinuclear species $[CGCTi(\mu\text{-}Me)_2AlMe_2]^+[MeMAO]^-$ (**4**).

In the $CGCMe_2/B(C_6F_5)_3$ system, only one Ti(III) species was observed. It was the reductive product of $[CGCTiMe]^+[MeB(C_6F_5)_3]^-$ (**6**). The Ti(III) concentration increased with the B/Ti molar ratio because the higher B/Ti molar ratio generated a higher **6** content. The results indicated that the binuclear cationic ion pair $[CGCTiMe(\mu\text{-}Me)MeTi\text{-}CGC]^+[MeB(C_6F_5)_3]^-$ (**7**) was stable to reduction. The $CGCTiMe_2/B(C_6F_5)_3$ system was much more stable to reduction compared to the $CGCTiMe_2$/MMAO system because of the higher stability of $[CGCTiMe]^+[MeB(C_6F_5)_3]^-$ (**6**).

The authors thank Prof. Qiang Yu, McMaster University, for his technical assistance in the ESR measurements, Dr. Youqing Shen for his helpful discussion, and the Natural Sciences and Engineering Council of Canada (NSERC) for the financial support for this research.

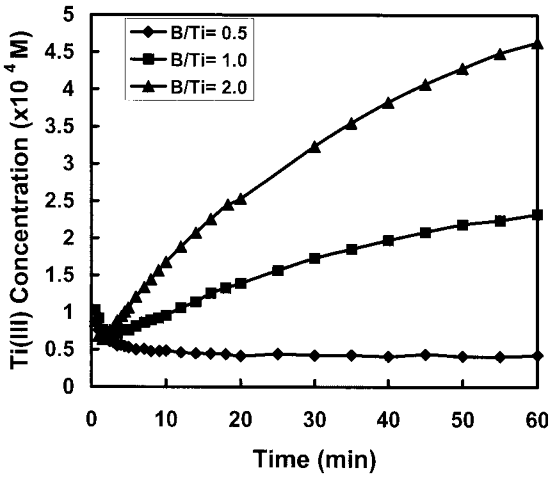


Figure 10 Ti(III) concentration versus time for the CGC-$TiMe_2/B(C_6F_5)_3$ system in toluene with different B/Ti molar ratios at $[Ti]_0 = 2 \times 10^{-2}$ *M* and T = 100°C.

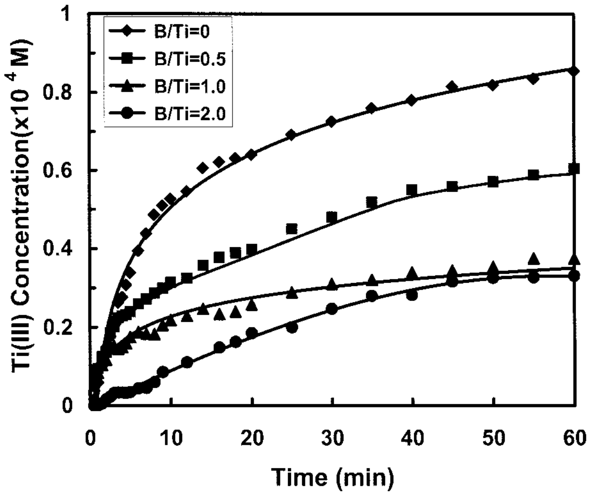


Figure 11 Ti(III) concentration versus time for the CGC-$TiMe_2/B(C_6F_5)_3$/MMAO system in toluene with different B/Ti molar ratios at $[Ti]_0 = 5 \times 10^{-4}$ *M*, Al/Ti = 20 (molar), and T = 100°C.

References

1. For recent reviews, see: (a) Kaminsky, W.; Arndt, M. Adv Polym Sci 1997, 127, 144; (b) Bochmann, M. J Chem Soc Dalton Trans 1996, 255; (c) Brintzinger, H.-H.; Fischer, D.; Mulhaupt, R.; Rieger, B.; Waymouth, R. M. Angew Chem Int Ed Engl 1995, 34, 1143; (d) Marks, T. J. Acc Chem Res 1992, 25, 57; (e) Jordan, R. F. Adv Organomet Chem 1991, 32, 325; (f) Chen, E. Y.-X.; Marks, T. J. Chem Rev 2000, 100, 1391.
2. Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Eur. Pat. 416815, 1997.
3. Canich, J. A. M. Eur. Pat. 788521, 1998.
4. Devore, D. D.; Timmers, F. J.; Hasha, D. L.; Rosen, R. K.; Marks, T. J.; Deck, P. A.; Stern, C. L. Organometallics 1995, 14, 3132.
5. Shapiro, P. J.; Cotter, W. D.; Schaefer, W. P.; Labinger, J. A.; Bercaw, J. E. J Am Chem Soc 1994, 116, 4623.
6. Shapiro, P. J.; Bunel, E.; Schaefer, W. P.; Bercaw, J. E. Organometallics 1990, 9, 867.
7. Lai, S.; Wilson, J. R.; Knight, G. W.; Stevens, J. C. U.S. Pat. 5,278,272, 1994.
8. Nickias, P. N.; Devore, D. D.; Timmers, F. J.; Rosen, R. K.; Mussell, R. D. U.S. Pat. 5,347,024, 1994.
9. Lindsay, K. F. Mod Plast 1993, October, 82.
10. Chum, P. S.; Kao, C. L.; Knight, G. W. Plast Eng 1995, June, 21.
11. Wang, W.-J.; Yan, D.; Charpentier, P. A.; Zhu, S.; Hamielec, A. E.; Sayer, B. G. Macromol Chem Phys 1998, 199, 2409.
12. Yan, D.; Wang, W.-J.; Zhu, S. Polymer 1999, 40, 1737.
13. McKnight, A. L.; Masood, M. A.; Waymouth, R. M.; Straus, D. A. Organometallics 1997, 16, 2879.
14. Olivé, G. H.; Olivé, S. Angew Chem Int Ed Engl 1967, 6, 790.
15. Bueschges, U.; Chien, J. C. W. J Polym Sci Polym Chem Ed 1989, 27, 1525.
16. Cam, D.; Sartori, F.; Maldotti, A. Macromol Chem Phys 1994, 195, 2817.
17. Huang, Y. H.; Yu, Q.; Zhu, S.; Rempel, G. L.; Li, L. J Polym Sci Polym Chem Ed 1999, 37, 1465.

18. (a) Grassi, A.; Pellecchia, C.; Oliva, L. Macromol Chem Phys 1995, 196, 1093; (b) Grassi, A.; Zambelli, A.; Laschi, F. Organometallics 1996, 15, 480; (c) Grassi, A.; Lamberti, C.; Zambelli, A.; Mingozzi, I. Macromolecules 1997, 30, 1884; (d) Grassi, A.; Saccheo, S.; Zambelli, A. Macromolecules 1998, 31, 5588.
19. Chien, J. C. W.; Salajka, Z.; Dong, S. Macromolecules 1992, 25, 3199.
20. Yim, J.-H.; Chu, K.-J.; Choi, K.-W.; Ihm, S.-K. Eur Polym J 1996, 32, 1381.
21. (a) Xu, J.; Zhao, J.; Fan, Z.; Feng, L. Macromol Rapid Commun 1997, 18, 875; (b) Xu, J.; Zhao, J.; Fan, Z.; Feng, L. Eur Polym J 1999, 35, 127.
22. Huang, Y. H.; Wang, W.-J.; Zhu, S.; Rempel, G. L. J Polym Sci Polym Chem Ed 1999, 37, 3385.
23. (a) Kucht, H.; Kucht, A.; Chien, J. C. W.; Rausch, M. D. Appl Organomet Chem 1994, 8, 393; (b) Ewart, S. W.; Sarsfield, M. J.; Jeremic, D.; Tremblay, T. L.; Williams, E. F.; Baird, M. C. Organometallics 1998, 17, 1502; (c) Ewart, S. W.; Sarsfield, M. J.; Williams, E. F.; Baird, M. C. J. Organomet Chem 1999, 579, 106; (d) Williams, E. F.; Murray, M. C.; Baird, M. C. Macromolecules 2000, 33, 261.
24. (a) Tritto, I.; Li, S.; Sacchi, M. C.; Zannoni, G. Macromolecules 1993 26, 7111; (b) Tritto, I.; Donetti, R.; Sacchi, M. C.; Locatelli, P.; Zannoni, G. Macromolecules 1997, 30, 1247; (c) Babushkin, D. E.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. Macromol Chem Phys 2000, 201, 558.
25. (a) Reddy, S. S.; Shashidhar, G.; Sivaram, S. Macromolecules 1993, 26, 1180; (b) Giannetti, E.; Nicoletti, G.; Mazzocchi, R. J Polym Sci Polym Chem Ed 1985, 23, 2117; (c) Chien, J. C. W.; Wang, B.-P. J Polym Sci Polym Chem Ed 1988, 26, 3089; (d) Cam, D.; Giannini, U. Makromol Chem 1992, 193, 1049.
26. (a) Gillis, D. J.; Tudoret, M.-J.; Baird, M. C. J Am Chem Soc 1993, 115, 2543; (b) Lancaster, S. J.; Robinson, O. B.; Bochman, M.; Coles, S. J.; Hursthouse, M. B. Organometallics 1995, 14, 2456.
27. Jia, L.; Yang, X.; Stern, C. L.; Marks, T. J. Organometallics 1997, 16, 842.
28. Chen, Y.-X.; Marks, J. Organometallics 1997, 16, 3649.