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ORIGINAL PAPER

A comparative study of ethylene polymerization by bis(aminotropone) Ti catalysts

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Abstract A series of titanium aminotropone complexes bearing a pair of chelating [O–N] ligands have been synthesized and used for polymerization of ethylene successfully. Ethylene polymerization reactions were carried out at different conditions using the prepared catalysts. The activities for ethylene polymerization were significantly dependent on the catalyst structure. The polymerization activity increased with increasing of the both monomer pressure and [MAO]:[Ti] ratio. The highest activity of the catalysts was obtained at about 30–40 °C. It was demonstrated that unlike the high performance Ti–FI catalysts, bis(aminotropone) Ti catalysts do not require the presence of steric bulk in close proximity to the oxygen moiety. Introduction of the bulky alkyl substitution next to the oxygen moiety decreased the activity of the catalysts. Density Functional Theory (DFT) studies reveal that the active species derived from these catalysts normally possess higher electrophilicity nature compared with those produced using bis(phenoxy-imine) Ti catalysts (Ti–FI catalysts). Hydrogen was used as the chain transfer agent. The activities of the catalysts were increased with hydrogen concentration to some extent, but the M_v values of the obtained polymers were decreased. Crystallinity and melting point of the obtained polymer were between 42–62% and 102–124 °C, respectively. Higher pressure increased both the crystallinity and the M_v values of the resulting polymers. The catalyst **8a** also produced PE with almost narrow polydispersities (1.10–2.55) as is typical for single-site catalysts. However, PDI was broadened by time.

Keywords Aminotropone · Ethylene polymerization · DFT studies

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Introduction

Since the pioneering by Karl Ziegler and Giulio Natta in the early 1950s on the polymerization of simple olefins, there has been intense interest in the application of early transition metal catalysts for the selective polymerization of inexpensive olefins [1]. Following Ziegler–Natta catalysts, metallocene catalysts were discovered in the 1980s and resulted in numerous industrial processes for improving the properties of polyolefinic materials along with performance parameters [2]. Recently, much more attentions have been devoted to the non-metallocene catalysts [3–7]. Design and synthesis of efficient transition metal catalysts toward precise, controlled olefin polymerization has attracted considerable attention [8–11].

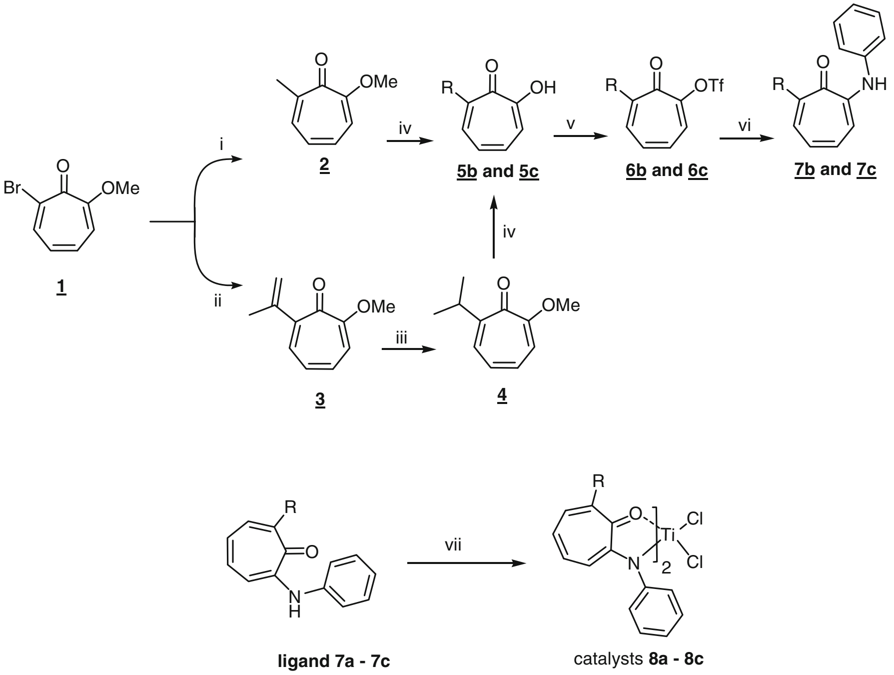
In consequence, quite a few highly active catalysts based on both early and late transition metal complexes have been developed [12–18]. There are, however, only a few examples of titanium complexes displaying high ethylene polymerization activities [19–22] though titanium metal is the major player in highly active heterogeneous Ziegler–Natta catalysts. Accordingly, we have conducted further research on titanium catalysts with the intention of developing the highly active titanium catalysts and applying them to polymerization of ethylene. Depending on the ligand design, the catalysts show different behaviors in ethylene and propylene polymerization, and the ligands strongly influence catalyst parameters such as activity, polymerization mechanism, and polymer properties including molecular weight [23].

A specific interest we have in mind is to find a high active catalyst and then investigate the electronic and steric effects of ligand on the catalyst behavior during the polymerization. As a result of ligand-oriented catalyst design research in our laboratories, we found out a new family of Ti complexes bearing two aminotropone chelate ligands, exhibiting high catalytic performance for ethylene polymerization (Scheme 1). Then, we prepared three different bis(aminotropone) Ti complexes by introducing alkyl substitutions on the catalyst structure to investigate the effects of catalyst structure on the catalyst activity and catalyst behavior during the polymerization as well as the characterization of the resulting polymer. Influence of hydrogen concentration on the polymerization activity was investigated. Also some specification of the resulting polymer was studied. Comparative experimental and theoretical study has been developed this contribution.

Experimental

Materials, ethylene polymerization, and characterizations

$TiCl_4$, cesium carbonate (Cs_2CO_3), tris(dibenzylideneacetone)dipalladium(0) (Pd_2dba_3), bis(diphenylphosphino)-1,1′-bipnaphtyl, aniline derivatives, alkylboronic compounds, HCl, trifilic anhydride, Na_2SO_4, NaH, MAO, and all solvents were supplied by Merck Chemical Co. (Darmstadt, Germany) and Fluka Co. and were used as received. The dried solvents were prepared from distilling over sodium wire, stored over 13X and 4A activated molecular sieves, and degassed by bubbling with dried nitrogen gas before



a: R = H.
b: R = methyl.
c: R = isopropyl.

i) $MeB(OH)_2$; ii) isopropenyl-$B(OH)_2$ and $Pd(Ph_3)_4$; iii) Pd/C and H_2; iv) HCl/MeOH; v) Tf_2O; vi) Pd_2dba_3, BINAP and $R'NH_2$; vii) NaH, $TiCl_4$

Scheme 1 Synthesis of ligands **7b** and **7c**, and catalysts **8a–c**

use. Polymerization grade ethylene (purity 99.9%) was supplied by Iranian Petrochemical Co. (Tehran, Iran). Nitrogen gas (purity 99.99%) was supplied by Roham (Tehran, Iran). Methylaluminoxane (MAO) (10% solution in toluene), and triisobutylaluminm (TIBA) (purity 93%) was supplied by Sigma Aldrich Chemicals (Steinheim, Germany). 2-Anilinotropone (**7a**) and 7-bromo-2-methoxytropone (**1**) were synthesized according to the literature [24].

NMR spectra were recorded on a Bruker BRX-500 AVANCE spectrometer at ambient temperatures. Chemical shifts for the ^{1}H NMR were referenced to an internal solvent resonance and reported relative to tetramethylsilane (TMS). Elemental analysis for CHN was carried out by the CHNO type from the Helaus Co. The elemental analysis for Ti was carried out using the ICP method by a SHIMADZU ICPS-8000 after dry ashing and dilutes nitric acid dissolution. Intrinsic viscosity (η) was measured in decalin at 135 °C using an Ubbelohde viscometer (polyethylene 25 mg/decalin 25 mL). Viscosity average molecular weight (M_v) values of polyethylenes were calculated from the following equation: $(\eta) = 6.2 \times 10^{-4}\ M_v^{0.7}$ [25]. Differential scanning calorimetry (DSC) (Universal V4IDTA) with a rate of

10 °C/min instrument was used for polymer characterization. According to the literatures [26, 27], calculation of $\Delta H_f/\Delta H_{f^*} \times 100$ gives the values of crystallinity of polyethylene, where ΔH_f is the heat of fusion which can be determined by DSC and $\Delta H_{f^*} = 69$ cal/g is the heat of fusion of 100% crystalline polyethylene.

Catalyst handling and polymerization procedures were carried out in 1-L stainless steel Buchi reactor (bcp 250) equipped with controllers systems as described before [28]. Toluene (250 mL) was introduced into the nitrogen-purged reactor and stirred (450 rpm), and the reactor was kept at the appropriate temperature and then the ethylene gas feed (100 L/h) was started. After 5 min, the ethylene gas feed was stopped, and the toluene solution was kept under N_2. To the resulting toluene solution were added toluene solutions of MAO and catalyst to start ethylene polymerization. Ethylene gas feed was started, and the pressure of reactor was kept constant at the applied monomer pressure for each run. After 15 min, isobutyl alcohol (10 mL) was added and reaction was terminated by shutting off the feed stream followed by nitrogen purge and polymer precipitation using acidified (HCl) methanol. The obtained polymer was recovered by filtration, washed with methanol (3 × 100 mL), and dried in a vacuum oven at 70 °C overnight.

General synthetic procedure for 7-substituted-2-methoxytropone compounds **2** and **3**

In a flask flushed with argon were placed the requisite amount of 7-bromo-2-methoxytropone (0.4 mmol), toluene (8 mL), and palladium tetrakistriphenylphosphine (0.04 mmol). A 2-M aqueous solution of sodium carbonate (0.4 mL, 0.8 mmol) and alkylboronic acid (0.44 mmol) dissolved in absolute ethanol (0.4 mL) were then sequentially added, and the mixture was heated at 100 °C for 16 h. Evaporation of the volatiles left a residue which was purified by chromatography on silica gel (eluent: hexane/ethyl acetate 9:1) [29].

*7-Methyl-2-methoxytropone (**2**)*

Compound **2** was obtained in 73% yield. ^{1}H NMR (CDCl$_3$, 500 MHz): $\delta = 2.44$ (s, 3H); 3.88 (s, 3H), 6.67 (d, 1H, $^3J = 9.2$), 6.70–6.86 (m, 1H), 6.91–7.04 (m, 1H), 7.32 (d, 1H, $^3J = 8.3$).

*7-Propenyl-2-methoxytropone (**3**)*

Compound **3** was obtained in 76% yield. ^{1}H NMR (CDCl$_3$, 500 MHz): 2.04 (m, 3H); 3.91 (s, 3H), 4.85 (m, 2H), 6.76 (d, 1H, $^3J = 9.4$), 6.70–6.87 (m, 1H), 6.90–7.02 (m, 1H), 7.30 (d, 1H, $^3J = 8.4$).

Preparation of 7-propyl-2-methoxytropone (**4**)

A solution of 7-Propenyl-2-methoxytropone (0.1 mol) in 150 cc of ethyl acetate is placed in the reaction bottle of the catalytic reduction apparatus, and 0.2 g of platinum oxide catalyst is added. The apparatus is evacuated, and then filled with hydrogen, and the mixture is shaken for 45 min. The platinum is filtered off, and the solvent is removed from the filtrate by distillation. The crude product was recrystallized from about 25 cc of alcohol. The yield was 76%. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.08$ (d, 6H, $^3J = 7.8$); 2.54 (m, 1H); 3.89 (s, 3H), 6.70 (d, 1H, $^3J = 9.5$), 6.72–6.83 (m, 1H), 6.93–7.00 (m, 1H), 7.34 (d, 1H, $^3J = 8.6$).

General synthetic procedure for 7-alkyltropolone compounds **5b** and **5c**

The starting 7-alkyl-2-methoxytropone (10 mmol) was dissolved in methanol (30 mL), and concentrated aqueous HCl (30 mL) was added. The resultant solution was refluxed for 6 h and allowed to cool slowly. The pure product crystallized out overnight [29].

*7-Methyltropolone (**5b**)*

Compound **5b** was obtained in 78% yield. ^{1}H NMR (CD_3OD, 500 MHz): $\delta = 2.55$ (s, 3H), 7.07 (td, 1H, $^4J = 1.4$, $^3J = 9.7$), 7.33–7.51 (m, 2H), 7.64 (d, 1H, $^3J = 9.1$).

*7-Propyltropolone (**5c**)*

Compound **5c** was obtained in 59% yield. ^{1}H NMR (CD_3OD, 500 MHz): $\delta = 1.13$ (d, 6H, $^3J = 7.8$), 2.62 (m, 1H), 7.11 (td, 1H, $^4J = 1.3$, $^3J = 9.5$), 7.30–7.48 (m, 2H), 7.61 (d, 1H, $^3J = 9.3$).

General synthetic procedure for 7-alkyl-2-triflatotropone compounds **6b** and **6c**

7-Alkyltropolone (5 mmol) was dissolved in pyridine (10 mL) and cooled to 0 °C. Triflic anhydride (5 mmol) was added dropwise, and the reaction mixture was warmed to room temperature and stirred overnight. The reaction mixture was diluted with water (100 mL) and extracted with diethyl ether (4×20 mL). The organic phase was washed with water (1×10 mL), 1 N HCl (2×10 mL), water (1×10 mL), and brine (1×10 mL) and dried over Na_2SO_4. The solvent was removed to yield crude product which was purified by column chromatography [30].

*7-Methyl-2-triflatotropone (**6b**)*

Compound **6b** was obtained in 45% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): 2.54 (m, 3H); 7.01 (t, 1H, $^4J = 1.3$, $3\ J = 9.7$), 7.34–7.51 (m, 2H), 7.55 (d, 1H, $^3J = 9.8$). ^{19}F NMR (CDCl3, 400 MHz): $\delta = -75.3$.

*7-Propyl-2-triflatotropone (**6c**)*

Compound **6c** was obtained in 39% yield. ^{1}H NMR ($CDCl_3$, 500 MH): $\delta = 1.15$ (d, 6H, $^3J = 7.8$), 2.50 (m, 1H), 7.17 (td, 1H, $^4J = 1.4$, $^3J = 9.3$), 7.33–7.47 (m, 2H), 7.62 (d, 1H, $^3J = 9.5$). ^{19}F NMR (CDCl3, 400 MHz): $\delta = -74.9$.

General synthetic procedure for 7-methyl-2-anilinotropone compounds **7b** and **7c**

A flame-dried Schlenk tube was charged with 7-methyl-2-triflatotropone (1.0 equiv.), Cs_2CO_3 (1.4 equiv.), Pd_2dba_3 (0.5 mol%), and racemic 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (1 mol%) under argon. Toluene (5 mL) and the appropriate aniline (1.2 equiv.) were added, and the reaction mixture was heated to 80 °C and stirred for 18–24 h. The reaction mixture was cooled to room temperature, diluted with diethyl ether, and filtered through Celite. The filtrate was concentrated and purified by flash chromatography on silica gel using 15% ethyl acetate in hexanes as the eluent [31].

*7-Methyl-2-anilinotropone (**7b**)*

Compound **7b** was obtained in 76% yield. ^{1}H NMR (CDCl3): $\delta = 2.52$ (s, 3H), 6.18 (d, $^3J = 10.4$, 1H), 6.41 (d, $^3J = 8.2$, 2H), 6.54 (t, $^3J = 7.8$, 1H), 6.69 (t, $^3J = 9.6$, 1H), 7.00 (dd, $^3J = 10.1$, 2H), 7.06 (t, $^3J = 10$, 1H), 7.30 (d, $^3J = 8.8$ Hz, 1H), 8.32 (br, s, NH). $C_{14}H_{13}NO$: Calcd. C 79.59, H 6.20, N 6.63; Found: C 79.50, H 6.17, N 6.56.

*7-Propyl-2-anilinotropone (**7c**)*

Compound **7c** was obtained in 59% yield. ^{1}H NMR (CDCl3): δ 1.14 (d, 6H, $^3J = 6.9$), 2.57 (m, 1H), 6.14 (d, $^3J = 10.4$, 1H), 6.41 (d, $^3J = 8.2$, 2H), 6.51 (t, $^3J = 7.8$, 1H), 6.71 (t, $^3J = 9.4$, 1H), 7.02 (dd, $^3J = 10$, 2H), 7.04 (t, $^3J = 10$, 1H), 7.35 (d, $^3J = 8.6$ Hz, 1H), 8.41 (br s, NH). $C_{17}H_{19}NO$: Calcd. C 80.60, H 7.56, N 5.53, Found: C 80.47, H 7.52, N 5.49.

General synthetic procedure for bis(Anilinotropone) Ti catalysts **8a–c**

To a stirred solution of appropriate ligand (3.0 mmol) in dried diethyl ether (20 ml) at −78 °C, NaH (10.0 mmol) was added. The solution was allowed to warm to room temperature and stirred for 2 h. The resulting solution was added dropwise over a 30-min period to a stirred solution of $TiCl_4$ (1.5 mmol) in dried diethyl ether (20 ml) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 15 h. The resulting mixture was concentrated in vacuo to give a solid, to which dried dichloromethane (20 ml) was added, and the mixture was stirred for 5 min. The resulting mixture was filtered, and then the residue was washed with dried dichloromethane. The combined organic filtrates were concentrated in vacuo to afford the crude complex. To the crude complex, dried diethyl ether (3 mL) and dried hexane (10 mL) were added and stirred for 15 min. A titanium complex was collected by filtration, washed with dried hexane, and dried in vacuo.

*Bis(2-anilinotropone) Ti complex (**8a**)*

73% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 6.31$–6.52 (m, 6H), 6.79–7.48 (m, 14H). $C_{26}H_{20}Cl_2N_2O_2Ti$: Calcd. C 61.08, H 3.94, N 5.48, Ti, 9.36; Found: C 60.78, H 3.90, N 5.41, Ti 9.25. FD-MS: m/z = 510 (M^+).

*Bis[7-methyl-2-anilinotropone] Ti complexes (**8b**)*

62% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.61$ (s, 6H), 6.47–7.44 (m, 4H), 6.22–6.52 (m, 14H). $C_{28}H_{24}Cl_2N_2O_2Ti$: Calcd. C 62.36, H 4.49, N 5.19, Ti 8.88; Found: C 61.95, H 4.42, N 5.14, Ti 8.81. FD-MS: m/z = 539 (M^+).

*Bis[7-isopropyl-2-anilinotropone] Ti complex (**8c**)*

42% yield. ^{1}H NMR ($CDCl_3$, 500 MHz): $\delta = 1.21$ (m, 12H), 2.54–2.64 (m, 2H), 6.50–7.37 (m, 4H), 6.31–6.60 (m, 14H). $C_{33}H_{32}Cl_2N_2O_2Ti$: Calcd. C 64.55, H 5.42, N 4.71, Ti 8.04; Found: C 64.46, H 5.37, N 4.56, Ti 7.97. FD-MS: m/z = 594 (M^+).

Results and discussion

Bis(aminotropone) Ti complexes **8a–c** with a series of substituents (H, methyl, and isopropyl) adjacent to the carbonyl moiety were prepared and examined for ethylene polymerization (Scheme 1). The polymerization results could reveal information about the potential and properties of bis(aminotropone) Ti complexes for ethylene polymerization, and additional information about the effect of the substituent adjacent to the carbonyl on catalytic performance.

Among catalyst components, ligand plays a predominate role in polymerization process. During electron exchange between metal and monomer, ligand aids metal to balance its electron density with receiving electrons from the coordinated ethylene through metal and releasing electrons whenever required to facilitate ethylene insertion process (Fig. 1).

Accordingly, to obtain a highly active catalyst, existence of ligands with remarkable balance between their electron donating and withdrawing, which is evidenced by calculation of their energy gap between HOMO (the highest occupied

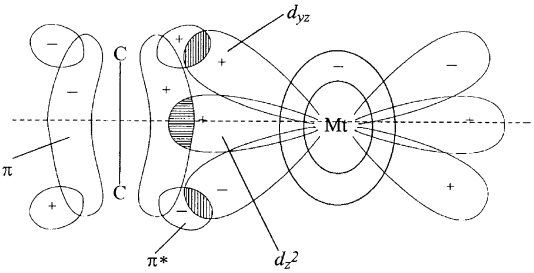
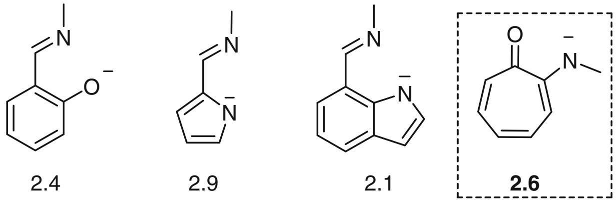


Fig. 1 Presentation of the olefin coordination on the transition metal



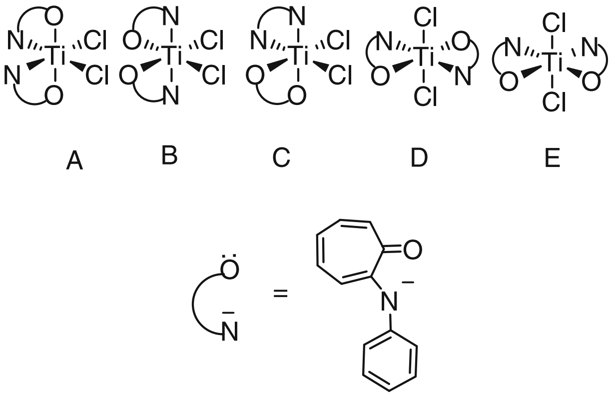
Scheme 2 Energy gap between HOMO and LUMO of aminotropone being compared with these related to phenoxy-imine, pyrrolide-imine, and indolide-imine (eV)

molecular orbital) and LUMO (the lowest unoccupied molecular orbital), is a predominate requirement [24, 32].

For comparison, the energy gap between HOMO and LUMO of three well-known ligands, i.e., phenoxy-imine [33–40], pyrrolide-imine [22], indolide-imine [41, 42], and the new aminotropone chelate ligand which has been prepared in this study was studied using DFT calculation. Because of the reasonable energy gap between HOMO and LUMO of aminotropone (2.6 eV), it was theoretically offered as a fundamentally active ligand (Scheme 2).

Since a bis(aminotropone) Ti catalyst contains a pair of non-symmetric bidentate ligands, it potentially displays five isomers (A–E) arising from the coordination modes of the two ligands in an octahedral geometry (Scheme 3). DFT studies suggest that bis(aminotropone) Ti catalyst **8a** assumes isomer A, with a *trans*-carbonyl-Os, *cis*-amine-Ns, and *cis*-Cls disposition.

It is believed that complexation of fundamentally active ligands with transition metals might result in high-activity ethylene polymerization catalysts as long as any



Isomer	A	B	C	D	E
RFE(KJ/Mol)	0	24.9	8.5	53.6	65.3

Scheme 3 The relative formation energies of the isomers A–E for catalyst **8a**

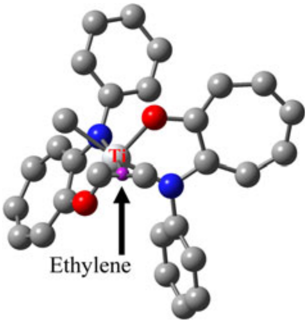
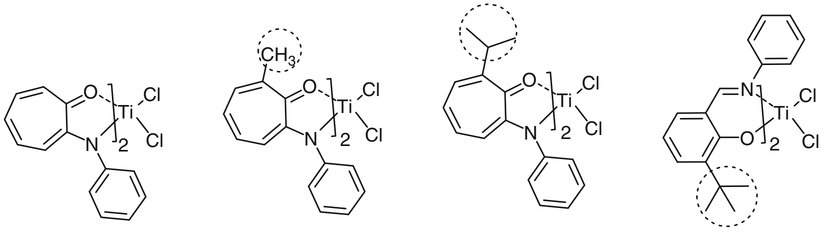


Fig. 2 Calculated structure of ethylene-coordinated cationic species derived from bis(aminotropone) Ti catalyst **8a**. The hydrogen atoms are omitted for clarity

cationic species derived from the resulting complexes has a pair of *cis*-located sites, which are needed for polymerization [22]. Therefore, DFT calculations were performed on a methyl cationic complex (an initial active species generated from bis(aminotropone) Ti catalyst **8a** with MAO) in the presence of ethylene, to obtain information about the structure of the catalytically active species (Fig. 2). The calculations reveal that an ethylene-coordinated cationic species assumes an octahedral geometry with a *trans*-carbonyl-Os, *cis*-amine-Ns, and *cis*-Me/coordinated ethylene disposition, which fulfills the pivotal requirement for a high efficient catalyst; i.e., a growing polymer chain and a coordinated-ethylene group in the *cis*-position. An inspection of the calculated structure indicates that the phenyl group on the amine-N is located in close proximity to the active site, suggesting that the substituent on the amine-N is the strategic substituent vis-à-vis catalyst design.

Then, we concentrated on the steric and electronic effects of the ligand on the catalyst performance in the experimental conditions. We found out that unlike bis(phenoxy-imine) Ti complexes (FI catalyst), which require steric bulk ortho to the phenoxy-O in order to exhibit high ethylene polymerization activity, activity of bis(aminotropone) Ti catalysts decreases with more congestion adjacent to the carbonyl Oxygen. The steric bulk in FI catalysts is thought to afford effective ion separation between the cationic active species and an anionic cocatalyst, resulting in enhancement of the catalytic activity. Accordingly, bis(aminotropone) Ti complex **8c**, which possess the isopropyl group showed lower activity than the other catalysts for ethylene polymerization under the conditions used (activity <100 kg-PE/mol-cat/h), while, bis(aminotropone) Ti catalyst **8a** with an H atom adjacent to the carbonyl afforded PE with a M_v of 260,000 and showed a high activity of 8000 kg-PE/mmol-cat/h. Additionally, catalyst **8b**, possessing the methyl group, exhibited almost moderate activity (activity: 3950 kg-PE/mol-cat/h). The activity obtained with complex **8a** (8000 kg-PE/mol-cat/h) is extremely high for a Ti complex with no Cp or PI ligand(s) [2, 32–40]. In fact, this activity exceeds that displayed by Ti–FI catalyst **8d**, [2-(Ph-NCH)-3-tBu-$C_6H_3O]_2TiCl_2$, under analogous conditions (3480 kg-PE/mol-cat/h) (Fig. 3) [32].

Regarding to lower HOMO–LUMO energy gap of FI type ligand (Scheme 2), we theoretically prognosticated a higher activity for Ti–FI catalyst **8d** compared with bis(aminotropone) Ti catalyst **8a**, but as can be seen in Fig. 3, an inverse result was obtained when these catalysts were experimentally used for polymerization of



Catalyst **8a**

8000 kg-PE/mmol cat/ h

Catalyst **8b**

3520 kg-PE/mol-cat/h

Catalyst **8c**

< 100 kg-PE/mol-cat/h

FI-Catalyst **8d**

3480kg-PE/mol-cat/h

Fig. 3 Investigation of substituent effects in bis(aminotropone) Ti complexes in comparison with a typical FI catalyst

ethylene. Furthermore, it has been known that the electronically flexible properties of ligands are a requirement for achieving high activity as long as a cationic species derived from a precatalyst complex possesses enough space for ethylene entry as well as an appropriate electron deficiency for fast coordination of ethylene with the metal center of complex [22]. Accordingly, DFT studies were employed on the active species derived from bis(aminotropone) Ti catalyst **8a** revealing a higher electrophilicity at the Ti center of corresponding catalyst compared with those of Ti–FI catalyst **8d** (Mulliken charge of the Ti in atomic unit, catalyst **8a** = 2.212, catalyst **8d** = 2.005), which could be a reasonable explanation for higher activity of catalyst **8a**. Additionally, the absence of a sterically demanding group adjacent to the carbonyl group might dedicate a sterically more open nature to catalyst **8a** compared with FI catalyst **8d**, facilitating access of ethylene to the unsaturated site of corresponding catalyst.

As discussed, unlike catalyst **8a**, catalysts **8b** and **8c**, with the methyl and isopropyl groups adjacent to the carbonyl-Os, display very low productivity in the polymerization of ethylene when compared with catalyst **8a**. The DFT optimized structures of methyl cationic complexes originating from **8a** and **8c** is displayed in Fig. 4. The isopropyl group of the complex **8c** seems to provide steric congestion near the polymerization center, which diminishes the rate of chain propagation. This is probably because it obstructs ethylene from gaining access to the active site and subsequent insertion into the Ti–carbon bond.

Comparative results of polymerization behavior of catalysts **8a–c**, Ti–FI catalyst **8d**, Cp_2TiCl_2, and Cp_2ZrCl_2 are presented in Table 1. The M_v values of the polymers obtained by the bis(aminotropone) Ti catalysts were increased as steric congestion next to the oxygen moiety were enhanced (entries 1–3). As a result, catalyst **8c**, possessing isopropyl group adjacent to the oxygen moiety afforded a polymer with the highest M_v value. The increase in M_v value of the obtained polymer using catalyst **8c** may be referred to the steric repulsion between β-hydrogen of growing polymer and bulky isopropyl substitution that could diminish β-hydride elimination through destabilization of β-agostic interaction. Less chain transfer reaction to the cocatalyst due to the bulky substitution is also conceivable.

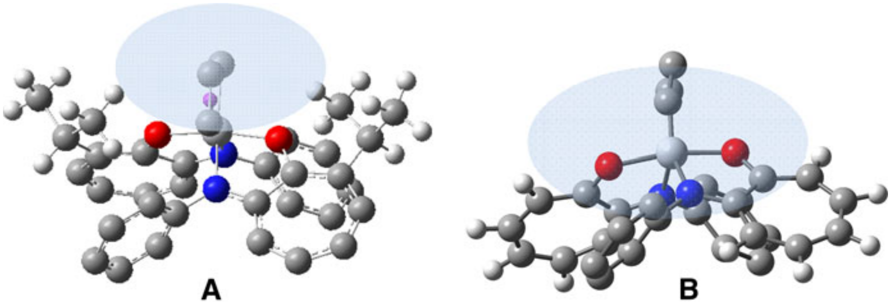


Fig. 4 Calculated structures of cationic active species generated from bis(aminotropone) Ti catalyst **8c** (**a**), bis(aminotropone) Ti catalyst **8a** (**b**). Some of the hydrogen atoms are omitted for clarity. For polymerization conditions see Table 1

In order to investigate the behavior of catalysts, ethylene polymerization was carried out at the various conditions. The activity of the catalyst, R_p (average) is expressed as kg-PE/(mmol-Ti/h). As expected, the activity of all the prepared catalysts, except **8c**, significantly increased as the [Al]/[Ti] molar ratio was enhanced (Fig. 5).

It has been known for FI catalysts that introduction of the bulky group next to the oxygen prevents the catalyst from coordination to the cocatalyst even at higher concentrations of cocatalyst and also induces effective ion-separation between the active species and anionic cocatalyst which leads to linear increase of its activity [37–40, 43]. In sharp contrast with FI catalyst, increasing MAO concentration could not dramatically affect the activity of the catalyst **8c**, possessing sterically demanding isopropyl group next to the oxygen (Fig. 5).

Requirement of great amount of MAO for catalysts **8a** and **8b** to exhibit higher catalytic activity can be explained by the equations which are shown in Fig. 6 [44]. Since MAO exists in large amount, MAO molecules may act as solvating molecules of the cation leading to separation of the ion pair (**3**). The new species, the metallic cation solvated by MAO, (**4**), is expected to be more active than the contact ion pair (**3**) and much more stable than the free cation solvated only by the solvent (toluene).

Table 1 Comparision of bis(aminotropone) Ti catalysts **8a–c**, FI catalysts **8d**, Cp_2TiCl_2, and Cp_2ZrCl_2

Entry	Catalyst	Activity (kg-PE/mol-cat/h)	M_v ($\times10^3$)[a]
1	**8a**	8000	260
2	**8b**	3520	271
3	**8c**	<100	352
4	**8d**	3480	368
5	Cp_2TiCl_2	16700	1253
6	Cp_2ZrCl_2	20000	1000

Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL

[a] Calculated from intrinsic viscosity

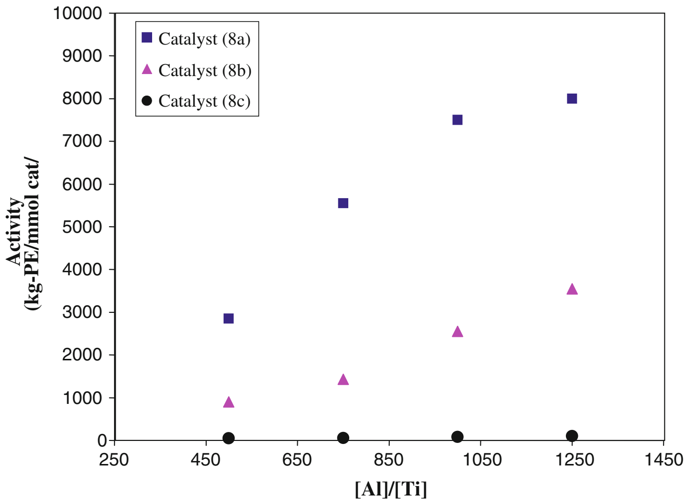


Fig. 5 Effect of MAO concentration on the catalyst activity. Polymerization conditions: temperature = 25 °C, polymerization time = 15 min, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL

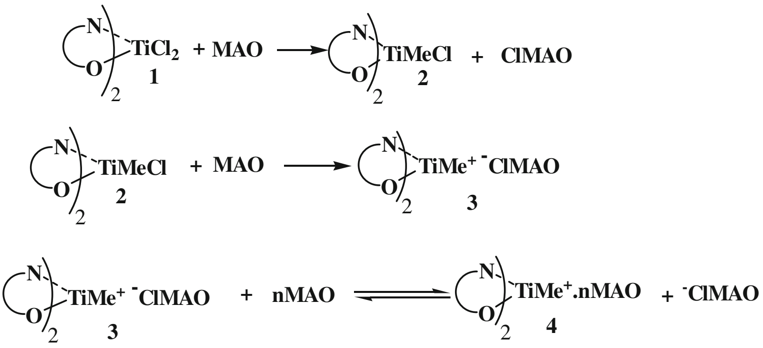


Fig. 6 Effect of MAO on ion pair separation and catalyst activation

This and the low value found for the equilibrium constant of the last equation may explain why the catalyst systems with MAO are much more active than those using alkylaluminium as cocatalyst and why such a large excess of MAO is necessary to obtain high activities.

As it is known, temperature has a major role in polymerization. The influence of polymerization temperature on activity was investigated at the temperatures between 25 and 50 °C, while the [Al]/[Ti] molar ratio was kept constant. As it can be seen in Fig. 7, the highest activity of the catalyst **8a** was obtained at 30 °C. However, the highest productivity of the catalysts **8b** and **8c** occurred at about 40 °C. The reduction in catalyst activity in the polymerization performed at the lower and upper temperatures than the optimum value could be attributed to a low

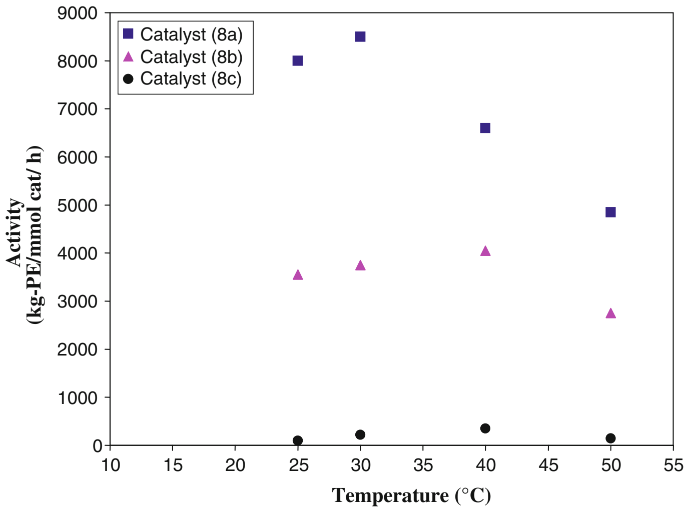


Fig. 7 Effect of temperature on the average rate of polymerization. Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL

propagation rate and catalyst irreversible deactivation, respectively [45]. The olefin polymerization rate is expected to increase with the temperature, but the trend is reversed at high temperature due to catalyst decomposition which occurs at high temperature. However, higher temperature promotes easy transfer of the monomer to the catalytic active centers [46]. Similar trends were already mentioned in the literature using homogeneous *ansa*-metallocene catalysts [25, 26, 47].

In general, higher monomer pressures increase activities rectilinearly, but because the catalytic behavior of the MAO activated bis(aminotropone) Ti catalysts is unique, the effect of pressure response was studied in the range 1 bars to 7 bars. The polymerization behavior is shown in Fig. 8. Due to high concentration of the monomer close to the catalyst active centers, the activity of all the prepared catalysts were raised with increasing the monomer pressure.

Hydrogen was used as a chain transfer agent, while the polymerization was carried out at the optimum conditions established before. The large amount of hydrogen concentration could slightly increase the activity of the catalyst (Fig. 9). A reasonable explanation for this effect might be increase of homogeneity of polymerization system and return of catalytically less reactive species, such as those resulting from 2,1-insertions, to the catalytic cycle through their fast hydrogenation [48].

Additionally, increasing concentration of hydrogen decreased the M_v values of obtained polymers using catalysts **8a–c** to some extent (Fig. 10). Enhanced concentration of hydrogen seems to accelerate associative chain transfer to the hydrogen, resulting in decrease of the M_v values.

The molecular weight distributions of some polyethylene samples were determined using the GPC method. As it can be seen in Fig. 11, polydispersity of

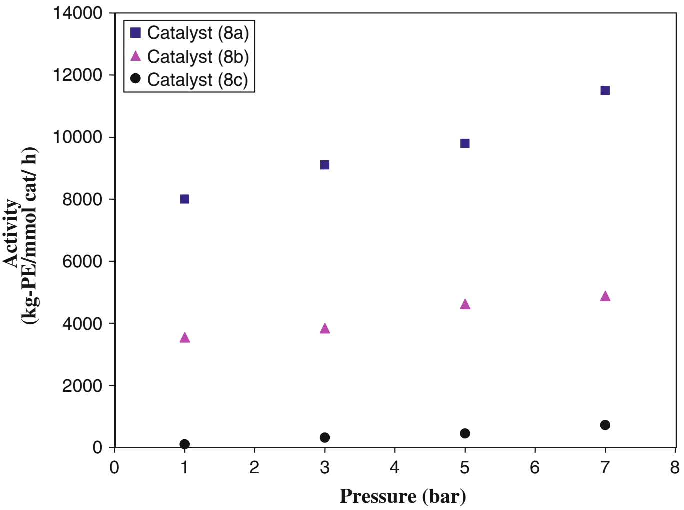


Fig. 8 Effect of pressure on the catalytic activity. Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, temperature = 25 °C, [Ti] = 1 mmol, toluene = 250 mL

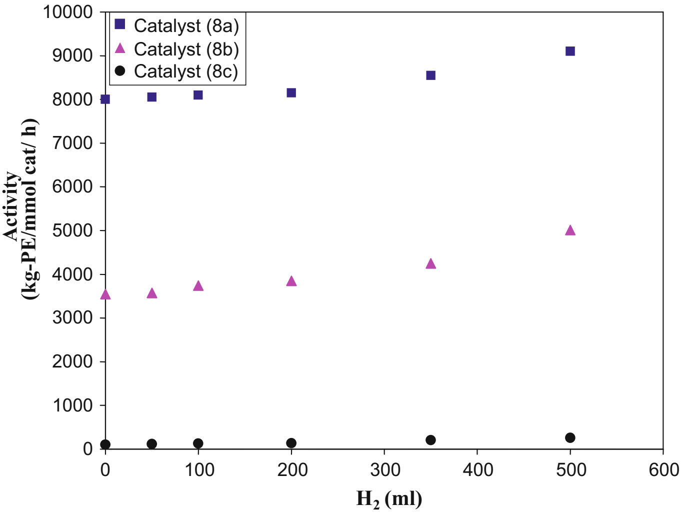


Fig. 9 Influence of H_2 concentration on the catalyst activity. Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL

the polymer obtained using the catalyst **8a** increases with time which indicates that the system starts to deviate from pure living manner. The reason can be that either the catalyst is not truly living over the full polymerization time or that the single-site system turns into a multi-site system due to heterogenization of the system. This would profoundly influence diffusion of ethylene to the living active centers. This

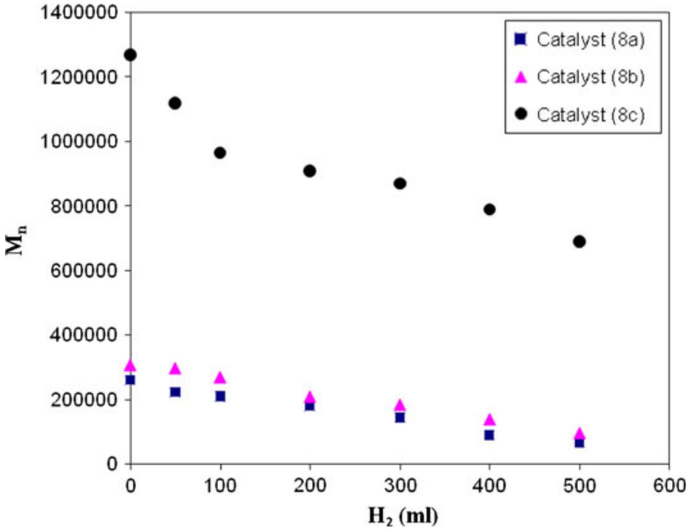


Fig. 10 Effect of hydrogen concentration on M_n. Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL

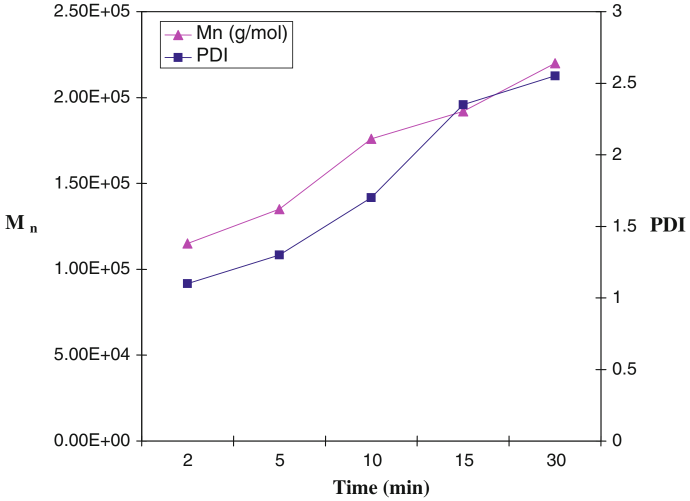


Fig. 11 PDI and M_n versus time for the polymer obtained by catalyst **8a**. Polymerization conditions: [Al]/[Ti] = 1250, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL. M_n and PDI were obtained from GPC

phenomenon could be comparable with self-immobilization of single-site catalysts that has been a subject of interest recently [49]. Similar result has been reported already by Ivanchev et al. [50]. The capture and blocking of active sites by the grown polymer after a certain polymerization time have been suggested. However, for short reaction times, a linear relationship between the polymerization time and the molar weight was observed.

Eventually, we investigated the effect of ethylene pressure, temperature, and [MAO]:[Ti] molar ratio on the crystallinity, melting point, and M_v values of obtained polymers using catalysts **8a–c** which has been presented in Table 2. At the same conditions, the polyethylene obtained by catalyst **8c** owned the highest

Table 2 Characterization of obtained polymer obtained by catalysts **8a–c**

Catalyst	Pressure	Temperature	[MAO]:[Ti]	Crystallinity (%)[a]	T_m (°C)	M_v ($\times 10^3$)[b]
8a	1	25	1250	48	105	260
8a	1	30	1250	51	108	240
8a	1	40	1250	42	102	229
8a	1	50	1250	50	110	213
8b	1	25	1250	47	104	271
8b	1	30	1250	44	104	265
8b	1	40	1250	54	109	246
8b	1	50	1250	46	101	234
8c	1	25	1250	55	115	352
8c	1	30	1250	57	112	347
8c	1	40	1250	59	117	339
8c	1	50	1250	58	111	330
8a	3	25	1250	48	105	278
8a	5	25	1250	51	108	342
8a	7	25	1250	54	114	351
8b	3	25	1250	49	104	314
8b	5	25	1250	52	111	372
8b	7	25	1250	55	114	380
8c	3	25	1250	57	115	340
8c	5	25	1250	61	121	445
8c	7	25	1250	64	126	475
8a	1	25	1000	50	116	270
8a	1	25	750	44	119	286
8a	1	25	500	46	120	301
8b	1	25	1000	47	114	288
8b	1	25	750	50	122	314
8b	1	25	500	43		326
8c	1	25	1000	57		369
8c	1	25	750	62		390
8c	1	25	500	62		418

Polymerization conditions: [Al]/[Ti] = 1250, polymerization time = 15 min, temperature = 25 °C, monomer pressure = 1 bar, [Ti] = 1 mmol, toluene = 250 mL

[a] Crystallinity (%) = $\Delta H_f/\Delta H_{f^*} \times 100$ where ΔH_f (obtained from DSC) is the heat of fusion and $\Delta H_{f^*} = 69$ cal/g is the heat of fusion of 100% crystalline polyethylene

[b] Calculated from intrinsic viscosity

crystallinity, melting point, and M_v values. Higher pressure increased melting point and crystallinity of the polymer obtained by catalysts **8a–c**. On the other hand, enhanced temperatures and greater amounts of [MAO]:[Ti] decreased the resulting polymer in M_v values, but their effect on the melting point and M_v values was not clear.

Conclusion

A new series of bis(aminotropone) Ti catalysts, which are based on nonsymmetric, electronically flexible aminotropone chelate ligands combined with Ti metal, has been synthesized and applied for ethylene polymerization. Upon activation with MAO, bis(aminotropone) Ti catalysts display high ethylene polymerization activities without any bulky alkyl substituents adjacent to the catalytic active centers. The polymerization reactions have been investigated at the different conditions precisely. We demonstrated that the catalyst performance during the polymerization can be affected by the ligand structure remarkably. DFT studies suggest that the catalytically active cationic species originating from these catalysts possesses a highly electrophilic nature when compared with FI catalysts. The highest activity demonstrated by a bis(aminotropone) Ti catalyst is comparable with those reported for FI catalysts at the similar conditions. A molecular weight distribution of 1.07–2.75 was obtained under the polymerization condition used. The polydispersity was broadened with time.

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