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Titanium precatalysts bearing *N*-substituted β-amino alcohols for 1-hexene polymerization: The effect of steric crowding

Kari Vijayakrishna, Govindarajan Sundararajan *

Department of Chemistry, Indian Institute of Technology Madras, Chennai 600 036, Tamil Nadu, India

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Abstract

A series of titanium-based non-metallocene precatalysts [2-(2,6-dialkylphenylamino)-1-phenylethoxy $TiCl_2$ were prepared by reacting lithium salts of the corresponding amino alcohols with $TiCl_4(THF)_2$. Upon activation with methylaluminoxane (MAO), these precatalysts polymerized 1-hexene in isotactic manner. The catalyst activity and polymer properties depended on the steric features in the ortho positions of the aniline moiety of the ligands. As the bulkiness of the alkyl group in ortho positions of the aniline moiety increased, the catalyst showed better activity with high molecular weight and greater tacticity control. For 1-hexene polymerization, precatalyst **1ATiCl$_2$** showed activity of 3.05 kg of PH/mol-Ti.h at room temperature and the resulting polyhexene had molecular weight of 403,600 ($M_w/M_n = 1.40$) with 80% isotacticity (*mmmm*). The dibenzylic titanium complexes **1ATi(CH$_2$Ph)$_2$** and **3ATi(CH$_2$Ph)$_2$**, upon activation with MAO or $Ph_3CB(C_6F_5)_4$, showed relatively lower activities towards 1-hexene polymerization, yielding polymers of lower molecular weights but with narrow molecular weight distribution.

Keywords: Non-metallocene catalyst; 1-Hexene polymerization; Isotactic

1. Introduction

Steric and structural changes in the ligand skeleton can have a big influence on the behavior of metallocene-based catalysts used in ethylene and propylene polymerization as well as cyclo-olefin copolymerization studies [1]. The last two decades, non-Cp type homogeneous catalysts have gained much attention in both industries and in academics as potential olefin polymerization catalysts [2]. Some of these catalysts polymerize olefins in living manner. These living olefin polymerization techniques allow the synthesis of wide variety of polymers, such as mono-dispersed, high molecular weight and block co-polymers [3,4]. However, it should be noted that better stereospecific polymers are obtained usually with metallocene catalysts when compared to non-Cp type catalyst systems. On the other hand, the usage of metallocene catalysts for polymerization of higher α-olefins is limited due to not-so-high catalytic activities as well as because of the low molecular weights of the polymers produced possibly because polymerization reactions by metallocene catalysts are plagued by chain termination and transfer steps [5]. In order to answer these queries, in non-metallocene catalysts, different types of chelating ligands are employed that has led to the discovery of remarkably active olefin polymerization catalysts [4,6]. It has been recognized that steric crowding around the metal center plays a crucial role in controlling the activity of the catalyst and in turn the stereoregularity and molecular weight of the polymers produced [7–12]. For instance, steric changes in the ligand skeleton can affect directly the stereochemical properties of the resulting polymer [6,7]. Recently, Kol et al. [7a] synthesized group IV diamine bis(phenolate) precatalysts wherein the dibenzylzirconium complex of a ligand with *ortho* *t*-butyl substituents on the phenolate rings led to living and isotactic polyhexene (PH). When they reduced the bulk of the ligand by replacing *ortho* *t*-butyl with methyl groups of the phenolate led to the loss of tacticity albeit with twofold increment in the catalytic activity. Here, they observed that in the zirconium catalysts bulky phenolate substituents are required for tacticity control.

In our laboratory, we have studied the role of molecular symmetry in 1-olefin polymerization with precatalysts bearing C_2 and C_3-symmetric ligands [13]. For instance, the aminodiolate based titanium precatalysts having C_2-symmetry produced high molecular weight isotactic PH while the C_s-meso catalyst produced only oligomers [13a]. Similarly, the C_3-symmetric aminotriolate titanium catalyst showed

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* Corresponding author. Tel.: +91 44 22574213; fax: +91 44 22574202.
E-mail address: gsundar@iitm.ac.in (G. Sundararajan).

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better activity for olefin polymerization compared to C_2 analogue [13b,c]. In this paper, we have extended the studies with titanium-based precatalysts containing C_1-symmetric *N*-substituted β-amino alcohols for 1-hexene polymerization.

Earlier, Rausch et al. [14] have synthesized two Ti(IV) complexes of the type $[(OCHRCH_2N\text{-}2,6\text{-}Me_2Ph)Ti(NMe_2)_2]_2$ (where R = H or *t*-butyl) by protonolysis of $Ti(NMe_2)_4$ with the ligands containing 2,6-dimethylaniline substituted amino alcohols. They reported that these precatalysts in the presence of excess of MAO polymerized ethylene, but under identical conditions failed to polymerize propylene.

In this paper, we summarize the results of our studies on the synthesis of various aminoalcohol ligands **1AH**$_2$, **2AH**$_2$, **3AH**$_2$ and **1BH**$_2$ (Scheme 1), and the precatalysts 2-(2,6-dialkylphenylamino)-1-phenylethoxy $TiCl_2$ [alkyl = isopropyl (**1ATiCl**$_2$), ethyl (**2ATiCl**$_2$), methyl (**3ATiCl**$_2$)] and 2-(2,6-diisopropylphenylamino)-2-phenylethoxy $TiCl_2$ (**1BTiCl**$_2$) derived from them (Scheme 2). The precatalysts when activated by MAO polymerize 1-hexene stereospecifically and these results will be discussed here.

2. Experimental section

2.1. Materials and general considerations

All reactions were carried out under dry and oxygen-free nitrogen or argon using glove box or standard Schlenk techniques. Transfers were performed in a glove box containing inert atmosphere or by standard syringe techniques. Solvents were distilled from sodium/benzophenone ketyl (hexane, toluene and THF) or P_2O_5 (CH_2Cl_2 and chlorobenzene) under nitrogen prior to use. 1-Hexene purchased from Aldrich Chemicals was distilled over calcium hydride and used. *n*-BuLi (1.6 M in hexane), Ph_3CCl, BCl_3 (1 M in hexane), $C_6H_5CH_2Br$, C_6F_5Cl and $TiCl_4$ were obtained from Aldrich Chemicals and used as received. MAO was purchased as 10% by weight solution in toluene from Witco GmbH, Germany and was used after estimating the aluminum content. ^1H NMR (400 MHz) and ^{13}C NMR (100 MHz) spectra were recorded using Bruker AV-400 spectrometer or Jeol GSX-400 spectrometer. ^{13}C NMR spectra of PH were recorded under quantitative conditions with pulse angle = 25°, pulse width = 2.8 μs, acquisition time = 0.655 s, relaxation time = 6 s and number of scans = 3000. Molecular weights of the PHs were determined by Waters GPC instrument with Styragel® columns (10^6, 10^5 and 10^3 Å columns connected in series) equipped with a RI detector using THF as solvent at a flow rate of 1.0 mL/min. Semi-preparative separation of ligand regioisomers were done in Shimadzu (LC-8A) HPLC instrument equipped with UV detector (SPD-6A) at 254 nm and ODS column using $MeOH{:}H_2O = 80{:}20$ solvent system at a flow rate of 10 mL/min. The IR spectra were recorded on Perkin–Elmer spectrum one FT-IR spectrometer model L120. Elemental analysis was carried out on a Perkin–Elmer 2400 model CHNS analyzer.

2.2. Synthesis of ligands

2.2.1. Synthesis of 2-(2,6-diisopropylphenylamino) 1-phenylethanol [*1AH*$_2$]

n-BuLi (1.6 M, 16.4 mL, 26.2 mmol) was added dropwise to a solution of 2,6-diisopropylaniline (4.60 g, 26 mmol) in THF at −78 °C over a period of 30 min, warmed to room temperature and stirred for 4 h. The reaction mixture was then cooled to −78 °C and styrene oxide (3.12 g, 26 mmol) was added dropwise. After addition, the solution was allowed to warm to room temperature and stirred for 3 h. The volatile materials from the reaction mixture were removed under reduced pressure and the residual mass was extracted with hexane (3×25 mL). Upon solvent evaporation, the reaction mixture provided crude product, which was purified by column chromatography (60–120 mesh silica gel) to give a mixture of regioisomers **1AH**$_2$ and **1BH**$_2$ in 90:10 ratio. Semi-preparative HPLC was employed to separate these two regioisomers. Final yield of **1AH**$_2$ = 72%.

For spectral data see Ref. [15].

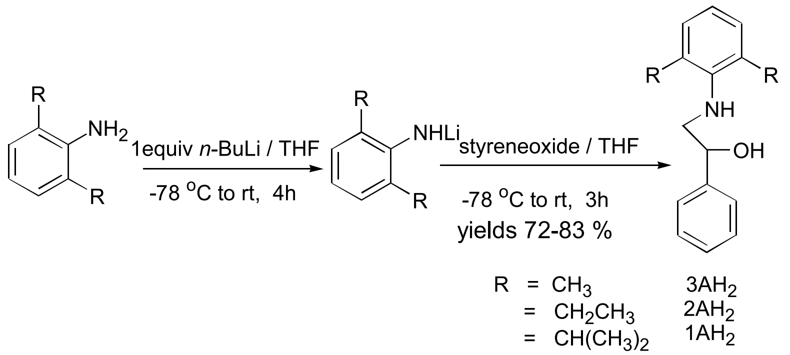
2.2.2. Synthesis of ligand *1BH*$_2$

For synthesis procedure and spectral data see Ref. [15].

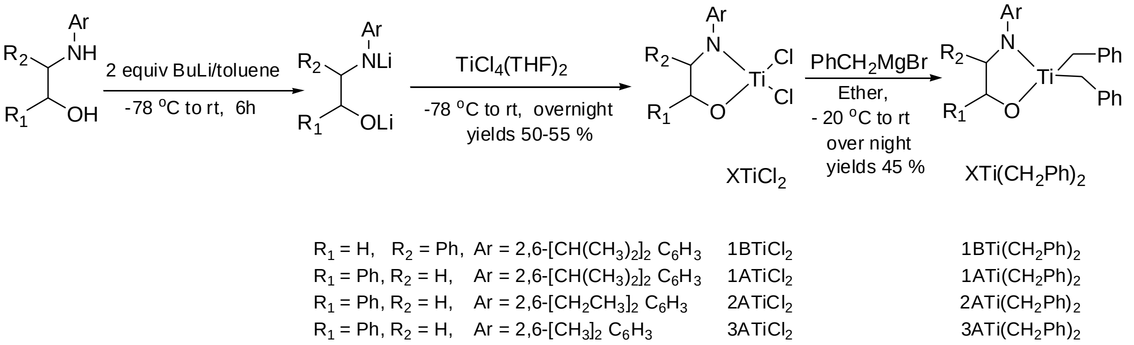
2.2.3. Synthesis of ligand *2AH*$_2$

2AH$_2$ was synthesized using a procedure as that employed for **1AH**$_2$. Final yield = 78%.

Nature: colorless viscous liquid; ^1H NMR (400 MHz, $CDCl_3$): δ 7.38–6.93 (m, 8H, Ar), 4.86 (dd, *J* = 8.1, 3.7 Hz, 1H, C*H*–CH_2), 3.20 (dd, *J* = 12.0, 3.7 Hz, 1H, C*H*H–CH), 3.10



Scheme 1. Synthesis of ligands 1-3AH$_2$.



Scheme 2. Synthesis of precatalysts.

(dd, $J=8.1$, 12.0 Hz, 1H, CH*H*–CH), 2.99 (br s, 2H, O*H*, N*H*), 2.65–2.59 (m, 4H, C*H*$_2$–CH$_3$), 1.20 (t, $J=7.5$ Hz, 6H, C*H*$_3$–CH$_2$); ^{13}C NMR (100 MHz, CDCl$_3$): δ 144.1, 142.2, 136.8, 128.5, 127.9, 126.7, 125.8, 123.2, 73.4, 57.2, 24.3, 14.8; HRMS calculated for $(M+H)=270.1858$, found $=270.1844$. Anal. Calcd for $C_{18}H_{23}NO$: C, 80.25; H, 8.60; N, 5.19. Found: C, 80.58; H, 8.67; N, 5.04.

2.2.4. Synthesis of ligand **3AH$_2$**

3AH$_2$ was synthesized using a procedure as that employed for **1AH$_2$**. Final yield = 83%.

Nature: colorless viscous liquid; ^{1}H NMR (400 MHz, CDCl$_3$): δ 7.46–6.88 (m, 8H, Ar), 4.89 (dd, $J=8.4$, 3.6 Hz, 1H, C*H*–CH$_2$), 3.32 (dd, $J=12.6$, 3.6 Hz, 1H, C*H*H–CH), 3.19 (dd, $J=12.6$, 8.4 Hz, 1H, CH*H*–CH), 2.80 (br s, 2H, O*H*, N*H*), 2.30 (s, 6H, C*H*$_3$-Ar); ^{13}C NMR (100 MHz, CDCl$_3$): δ 145.4, 142.5, 130.0, 129.1, 128.8, 128.1, 126.1, 122.6, 73.5, 55.8, 18.6; HRMS calculated for $(M+H)=242.1545$, found $=$ 242.1534. Anal. Calcd for $C_{16}H_{19}NO$: C, 79.63; H, 7.93; N, 5.80. Found: C, 80.02; H, 8.17; N, 5.84.

2.3. Preparation of complexes

2.3.1. Preparation of **1ATiCl$_2$** complex

n-BuLi (1.6 M, 4.5 mL, 7.2 mmol) was added dropwise to a stirred toluene solution of β-amino alcohol 1AH$_2$ (1.03 g, 3.50 mmol) at −78 °C, warmed to room temperature and stirred for 6 h, TiCl$_4$(THF)$_2$ (1.23 g, 3.6 mmol) was added at −78 °C. The solution that turned green immediately and then to deep brown, was allowed to warm to room temperature and stirred for 16 h. The volatile materials from the reaction mixture were removed under vacuum and the residual mass was extracted with dichloromethane and reprecipitated in hexane as brown colored powder. The precipitate when filtered, washed with hexane and dried under vacuum afforded deep brown powder.

Nature: brown powder; ^{1}H NMR (400 MHz, CDCl$_3$): (broad peaks are observed in each case) δ 7.44–7.16 (8H, Ar), 5.85 (1H, C*H*–CH$_2$), 3.60 (2H, C*H*$_2$–CH), 3.16 (2H, C*H*(CH$_3$)$_2$), 1.28 (12H, CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{20}H_{25}NOTiCl_2$: C, 57.99; H, 6.08; N, 3.38. Found: C, 58.16; H, 6.20; N, 3.48.

2.3.2. Preparation of **1BTiCl$_2$** complex

1BTiCl$_2$ was synthesized using the same procedure as that employed for **1ATiCl$_2$**.

Nature: brown powder; ^{1}H NMR (400 MHz, CDCl$_3$): (broad peaks are observed in each case) δ 7.44–7.03 (8H, Ar), 4.80 (3H, C*H*–C*H*$_2$), 3.08 (2H, C*H*(CH$_3$)$_2$), 1.34 (12H, CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{20}H_{25}NOTiCl_2$: C, 57.99; H, 6.08; N, 3.38. Found: C, 57.81; H, 6.22; N, 3.56.

2.3.3. Preparation of **2ATiCl$_2$** complex

2ATiCl$_2$ was synthesized using the same procedure as that employed for **1ATiCl$_2$**.

Nature: brown powder; ^{1}H NMR (400 MHz, CDCl$_3$): (broad peaks are observed in each case) δ 7.52–7.02 (8H, Ar), 5.85 (1H, C*H*–CH$_2$), 3.65 (2H, C*H*$_2$–CH), 3.12 (4H, C*H*$_2$–CH$_3$), 1.27 (6H, CH$_2$C*H*$_3$). Anal. Calcd for $C_{18}H_{21}NOTiCl_2$: C, 55.98; H, 5.48; N, 3.62. Found: C, 55.91; H, 5.52; N, 3.64.

2.3.4. Preparation of **3ATiCl$_2$** complex

3ATiCl$_2$ was synthesized using the same procedure as that employed for **1ATiCl$_2$**.

Nature: brown powder; ^{1}H NMR: (400 MHz, CDCl$_3$): (broad peaks are observed in each case) δ 7.43–7.15 (8H, Ar), 6.00 (1H, C*H*–CH$_2$), 3.57 (2H, C*H*$_2$–CH), 2.35 (6H, C*H*$_3$-Ar). Anal. Calcd for $C_{16}H_{17}NOTiCl_2$: C, 53.66; H, 4.78; N, 3.91. Found: C, 53.69; H, 4.83; N, 3.86.

2.3.5. Preparation of **1ATi(CH$_2$Ph)$_2$** complex

To a diethyl ether (50 mL) suspension of **1ATiCl$_2$** (0.250 g, 0.603 mmol) was added 2.2 equiv of PhCH$_2$MgBr (1.326 mmol) at −20 °C. The solution was warmed to room temperature and stirred overnight. The solvent was removed under vacuum and the solid was extracted with dichloromethane and precipitated in hexane. The precipitate was filtered, washed with hexane (2×25 mL) and dried under vacuum to afford 140 mg of product (44%) as yellow powder.

Nature: yellow powder; ^{1}H NMR (400 MHz, CDCl$_3$): (broad peaks are observed in each case) δ 7.48–7.19 (18H, Ar), 5.90 (1H, C*H*–CH$_2$), 3.65 (2H, C*H*$_2$–CH), 3.14 (2H, C*H*(CH$_3$)$_2$), 2.70 (4H, C*H*$_2$Ph), 1.32 (12H, CH(C*H*$_3$)$_2$). Anal. Calcd for $C_{34}H_{39}NOTi$: C, 77.70; H, 7.48; N, 2.67. Found: C, 77.87; H, 7.62; N, 2.89.

2.3.6. Preparation of *$\mathbf{3ATi(CH_2Ph)_2}$* complex

$3ATi(CH_2Ph)_2$ was synthesized using the same procedure as that employed for **$1ATi(CH_2Ph)_2$**.

Nature: yellow powder; ^1H NMR (400 MHz, $CDCl_3$): (broad peaks are observed in each case) δ 7.58–7.02 (18H, Ar), 5.87 (1H, $C\mathit{H}$–CH_2), 3.95 (1H, $C\mathit{H}$H–CH), 3.55 (1H, CHH–CH), 2.76 (4H, $C\mathit{H}_2$Ph); 2.33 (6H, $C\mathit{H}_3$–Ar). Anal. Calcd for $C_{30}H_{31}NOTi$: C, 76.76; H, 6.66; N, 2.98. Found: C, 77.17; H, 6.92; N, 3.12.

The borates, viz. $Ph_3CB(C_6F_5)_4$ and $B(C_6F_5)_3$, were prepared according to literature procedure [16].

2.4. 1-Hexene polymerization

2.4.1. General procedure

Fifty micromoles of precatalyst (in chlorobenzene as a stock solution) and required amount of MAO were added to a round bottomed flask (50 mL) and was stirred for 10 min. Two millilitres of 1-hexene was added to the above solution, stirred for prescribed time at required temperatures. Polymerization was quenched by adding acidified methanol and the polymer was extracted in chloroform, dried under vacuum.

2.4.2. Polymerization of 1-hexene catalyzed by *$\mathbf{1ATi(CH_2Ph)_2}$–$Ph_3CB(C_6F_5)_4$* and *$\mathbf{3ATi(CH_2Ph)_2}$–$Ph_3CB(C_6F_5)_4$* systems

Two millilitres of 1-hexene and 50 μmol of precatalyst (in chlorobenzene as a stock solution) were taken into a round bottomed flask (50 mL). The polymerization was started by adding 50 μmol $Ph_3CB(C_6F_5)_4$ and was stirred for prescribed time. Polymerization was quenched by adding acidified methanol and the polymer was extracted in chloroform, dried under vacuum.

3. Results and discussion

3.1. Preparation and characterization of the catalysts

The ligands **$1\text{-}3AH_2$** were synthesized by ring-opening of styrene oxide with monolithiated 2,6-dialkylaniline as shown in Scheme 1. Amino alcohols **$1\text{-}3AH_2$** were isolated as the major product on purification by semi-preparative HPLC and were characterized by IR, ^1H and ^{13}C NMR spectroscopy as well as by mass and elemental analyses. Structure of **$1AH_2$** was unambiguously confirmed by single crystal XRD [17]. **$1BH_2$** was synthesized as per known literature procedure [15]. The ligand was treated with 2 equiv of *n*-BuLi at −78 °C, that on reaction with $TiCl_4(THF)_2$ gave the required complex as a brown powder (Scheme 2). In the ^1H NMR spectrum of **$1AH_2$** (Fig. 1(a)), the two methylene protons, *N*-$C\mathit{H}_2$–CH(OH)-Ph appeared as two doublet of doublets at 3.05 and 3.24 ppm and the benzylic proton, Ph-$C\mathit{H}$(OH)–CH_2 appeared as a doublet of doublet at 4.95 ppm. The ^1H NMR of the complex **$1ATiCl_2$** (Fig. 1(b)) showed around 1 ppm downfield shift for benzylic proton, from 4.95 to 5.90 ppm and methylene protons shifted downfield (≈0.5 ppm) from 3.15 to 3.70 ppm indicative of the complex formation. Similar downfield shifts were observed for other complexes also. However, all our attempts to obtain single-crystal XRD of these complexes failed.

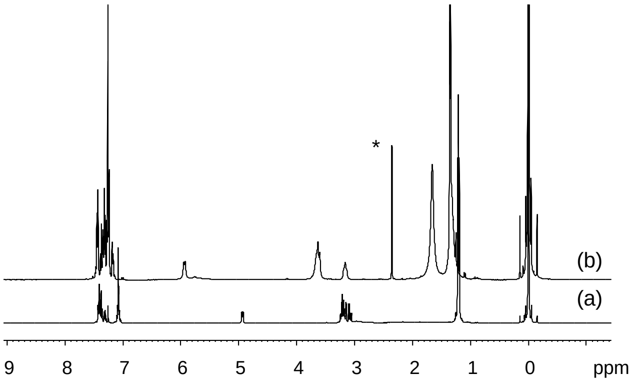


Fig. 1. ^1H NMR spectra of (a) **$1AH_2$** and (b) **$1ATiCl_2$** (*toluene solvent).

From the literature it is known that titanium based complexes do exist in dimeric and higher polymeric species through bridged oxygens [14,18–24]. Using NMR we opted to study the changes in the nature of the complex by adding coordinating solvents like THF and varying temperatures but could discern very little information. At this stage, though we are not clear about the nature of these complexes, we believe that the symmetry around the metal center in these complexes is C_1 irrespective of whether they exist in monomeric or dimeric form.

3.2. Polymerization of 1-hexene

These precatalysts were activated with MAO for polymerization of 1-hexene under different reaction conditions by varying temperature, Al/Ti ratio and the solvent. All the precatalysts, except **$1BTiCl_2$** showed moderate activity towards 1-hexene polymerization.

Catalyst activity was suppressed when toluene was used as solvent (**$1ATiCl_2$**—activity = 0.15 kg of PH/mol-Ti·h, M_n = 72,000, PDI = 1.70) attributable to competitive binding of toluene to cationic titanium active center as suggested by McConville et al. [12]. Though the catalyst showed improved catalytic activity in DCM and chlorobenzene, better activity was observed in neat conditions only.

Thus, under neat conditions, a linear relationship in modified Arrhenius plot ($\ln M_n$ vs $1/T$) was obtained for **$1ATiCl_2$** catalyst system (Fig. 2) suggesting the presence of a single active species in the polymerization process. To explore this aspect further, we employed a 1:1 mixture of precatalysts **$1ATiCl_2$/$3ATiCl_2$** for 1-hexene polymerization to yield PH that had a bimodal distribution in GPC. On closer scrutiny, the GPC traces of the polymers obtained from precatalysts **$1ATiCl_2$**, **$3ATiCl_2$**, and **$1ATiCl_2$/$3ATiCl_2$** implied the presence of a mixture of two different homopolymers in the mixed catalyst system. This would point to the fact that, in the **$1ATiCl_2$/$3ATiCl_2$** system, the precatalysts act individually without any interaction between the two different catalyst centers or for that matter aggregate to form a new catalytic system. As a verification experiment, we mixed **$1AH_2$** and **$3AH_2$** in equal amounts and complexed the mixture with $TiCl_4$

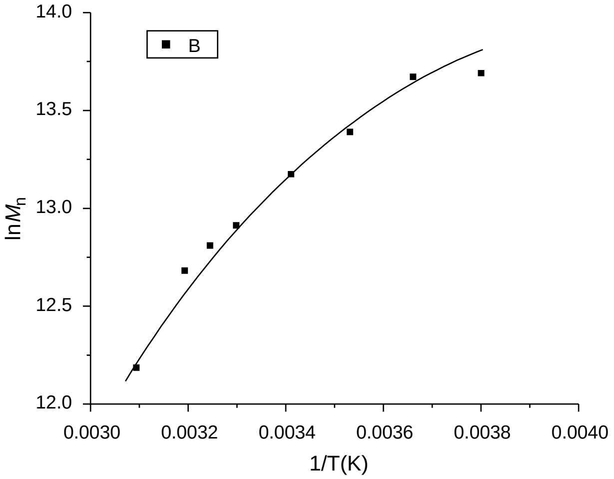


Fig. 2. Modified Arrhenius plot (ln M_n vs $1/T$) for **1ATiCl$_2$**/MAO catalyst system.

(THF)$_2$ to obtain **1A/3A-TiCl$_2$**. If the complexes were to exist in dimeric form, then three different possibilities arise, namely, **1A–1A**, **3A–3A** and **1A–3A**. If these dimeric precatalyts were active without cleaving into individual ones, then the **1A/3A-TiCl$_2$** system would generate in more than two active sites leading to a multimodal distribution in GPC but the PH obtained here also showed a bimodal distribution in the GPC that was highly similar to the one described earlier for polymers obtained from preactalyst **1ATiCl$_2$/3ATiCl$_2$** (Fig. 3). Hence, we speculate that the precatalysts, even if were to be in dimeric form, cleave into monomeric active species under the given reaction conditions [13b].

In the ^{13}C NMR spectra of PH prepared by these precatalysts, only the six peaks corresponding to six different carbons are observed. Keeping the signal of the C3 carbon as reference to calculate the relative intensities of pentads, we find the *mmmm* pentad to be more predominant suggesting isotactic nature [25]. Besides, the ^{13}C NMR of PH obtained from **1ATiCl$_2$**/MAO at -10 °C (Fig. 4), has $E=0.92$ that is close to one suggesting an enantiomorphic site control mechanism for propagation [26].

From the literature it is also known that very few non-metallocene systems induce higher tacticity in the resulting polymers. For example, C_s-symmetric zirconium complex of amino bis(phenolate)ligand gave atactic PH where as C_2-symmetric complex of amino bis(phenolate)ligand gave $>95\%$ isotactic PH [7c]. In these complexes, it has been suggested that in addition to the ligand symmetry around the metal centre, the size of the phenolate substituents also dictates the tacticity of the produced PH. PH synthesized from **1-3ATiCl$_2$**/MAO catalysts is amorphous at room temperature in compliance with the general observation that most of the isotactic PH are amorphous at room temperature [27].

3.3. *Effect of steric crowding*

The ligand environment around the metal center showed greater influence on catalyst activity. Thus, **1ATiCl$_2$** was active for 1-hexene polymerization, while **1BTiCl$_2$** did not polymerize 1-hexene, though the parent ligands **1AH$_2$** and **1BH$_2$** are regioisomers. We think this could be because, in **1BTiCl$_2$** the phenyl group is in β-position to oxygen with the metal centre being more exposed and hence less protected, resulting in a crowded environment upon addition of MAO. The metal center is then less accessible for bulkier monomers like 1-alkene, an observation made earlier for similar type of catalyst systems reported by Rausch et al. [14]. They also reported that when the amino alcohol having hydrogen in the α-position to the oxygen was replaced by *t*-butyl group the catalyst showed 10-fold increase in activity for ethylene polymerization at 25 °C. In the case of **1ATiCl$_2$** the phenyl group is at the α-position to the oxygen, thus metal centre was well protected and resulted in better activity towards 1-hexene polymerization. Thus, changing the position of phenyl group in the ligand strongly influenced the catalyst activity.

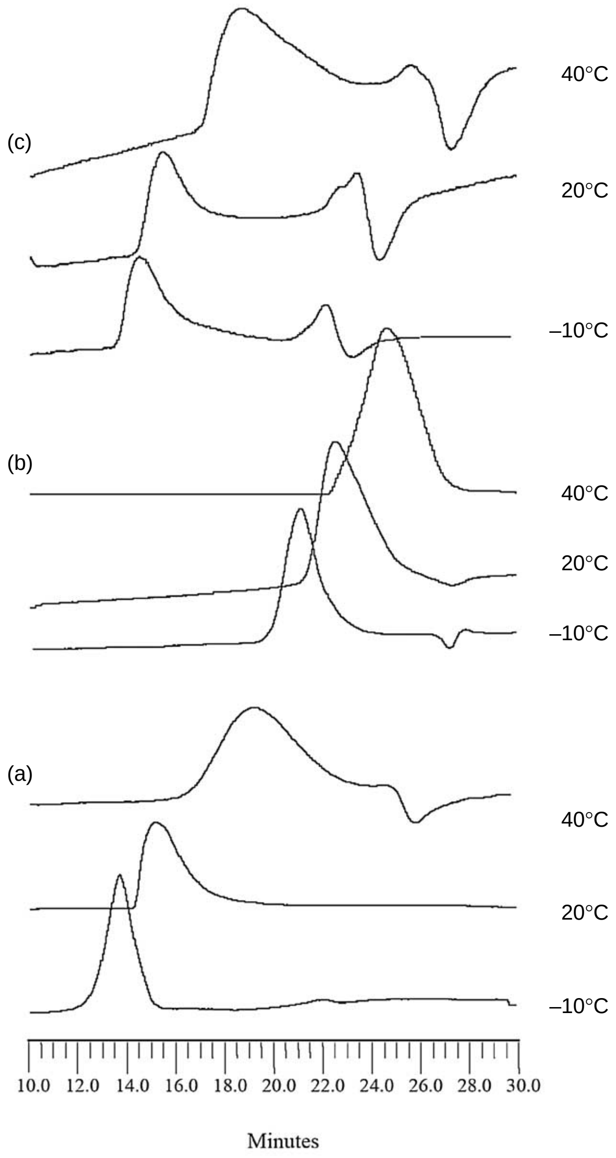


Fig. 3. GPC overlay of PH obtained with (a) **1ATiCl$_2$** (b) **3ATiCl$_2$** and (c) **1A/3A-TiCl$_2$** at different temperatures.

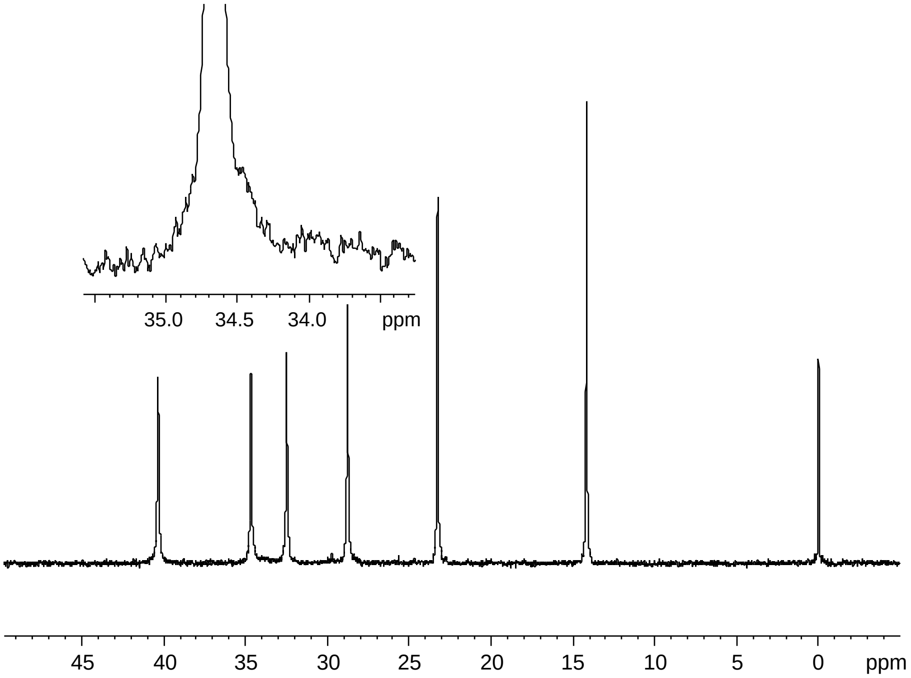


Fig. 4. ^{13}C NMR of PH obtained with **1ATiCl$_2$**/MAO at −10 °C. Inset: expanded signal representing the C3-carbon used for calculating the abundance of various sequences.

The polymerization data suggests that phenyl substitution in the α-position to oxygen in ligand is essential for effective catalysis for 1-hexene polymerization.

To understand the influence of substitution in the 2,6 position in the aniline moiety of ligand on catalyst activity and polymer properties, we have chosen three different catalyst systems (**1ATiCl$_2$**, **2ATiCl$_2$** and **3ATiCl$_2$**) for this study. These catalysts showed specific trends in their activities for 1-hexene polymerization and the results are given in Table 1 and 2. The environment around the metal center had greater influence on polymerization activity, molecular weight and tacticity of the obtained polymers. The catalyst activity for 1-hexene polymerization decreased in the order of **1ATiCl$_2$**> **2ATiCl$_2$**>**3ATiCl$_2$**. Similar trend was also observed for the molecular weight of the PH obtained with these precatalysts. Highest molecular weight for PH (entry 4, Table 1) was obtained with **1ATiCl$_2$** at −10 °C. It is clear that substituents in the 2,6 position in the aniline moiety in ligand plays a major role in the catalyst activity and polymer properties. Upon increasing the size of the ortho substituents of aniline moiety, molecular weights of the polymers increased significantly (Table 2). Bulky aryl substitutions in the precatalysts provide improved cation–anion separation of the active species thereby allowing more space for 1-hexene coordination to the metal center. The bulky ortho substituents could also provide steric protection to avoid electrophilic attack of the cocatalyst (MAO) on the active site leading to catalyst deactivation [28]. Another interesting observation is upon increasing the

Table 1
1-Hexene polymerization with **1ATiCl$_2$**/MAO at different temperatures[a]

Run	Al/Ti	Temperature	Activity[b]	M_n[c]	PDI[c]	% Isotacticity[d]
1	100	rt	0.14	128,000	1.55	72
2	300	rt	0.62	156,000	1.59	79
3	500	rt	0.34	124,600	1.72	85
4[e]	200	−10	1.45	878,000	1.07	90
5[e]	200	0	2.10	862,300	1.16	–
6[e]	200	10	2.84	650,000	1.20	–
7[e]	200	20	3.05	524,000	1.35	87
8[e]	200	rt	3.50	403,600	1.40	80
9[e]	200	35	4.25	364,000	1.59	–
10[e]	200	40	1.27	320,000	2.71	65
11[e]	200	50	0.79	195,000	2.93	60

[a] Polymerization conditions: 2 mL of 1-hexene; neat conditions, 50 μmol of precatalyst; 6 h polymerization period.
[b] Activity in kg-polymer/mol-Ti·h.
[c] From GPC data in THF vs polystyrene standards.
[d] From ^{13}C NMR.
[e] Dry MAO was used as cocatalyst for entries 4–11.

Table 2
1-Hexene polymerization at room temperature[a]

Run	Catalyst	Al/Ti	Activity[b]	M_n[c]	PDI[c]	% Isotacticity[d]
1	1ATiCl$_2$	100	1.48	381,600	1.32	77
2	1ATiCl$_2$	200	3.50	403,600	1.40	80
3	1ATiCl$_2$	400	1.40	312,500	1.45	85
4	2ATiCl$_2$	100	1.05	125,900	1.47	68
5	2ATiCl$_2$	200	1.45	154,800	1.48	73
6	2ATiCl$_2$	400	0.70	125,000	1.50	78
7	3ATiCl$_2$	100	0.75	56,700	1.48	65
8	3ATiCl$_2$	200	0.85	64,800	1.55	68
9	3ATiCl$_2$	400	0.35	48,300	1.52	75
10	1ATiBn$_2$	200	2.50	25,000	1.17	89
11[e]	1ATiBn$_2$	–	2.05	63,000	1.12	90
12	3ATiBn$_2$	200	0.45	12,000	1.15	87
13[e]	3ATiBn$_2$	–	0.40	27,500	1.10	89

[a] Conditions: 2 mL of 1-hexene; neat conditions, 50 μmol of precatalyst; 6 h polymerization period, dry MAO as cocatalysts for entries 1–10 and 12.

[b] Activity in kg-polymer/mol-Ti·h.

[c] From GPC data in THF vs polystyrene standards.

[d] From ^{13}C NMR.

[e] $Ph_3CB(C_6F_5)_4$ was used as cocatalysts for entries 11 and 13.

steric bulk of the ligand at the ortho positions by varying from methyl to ethyl to isopropyl groups an increase in the isotacticity of the resulting polyhexenes. Isotacticity of PH obtained at room temperature by these catalysts when employed with dry MAO, increases in the following manner **3ATiCl$_2$** (*mmmm* = 75%) < **2ATiCl$_2$** (*mmmm* = 78%) < **1ATiCl$_2$** (*mmmm* = 85%).

3.4. Effect of cocatalyst

Upon activation with MAO, precatalysts containing ligands **1-3AH$_2$** were found to be active for 1-hexene polymerization. In order to study the effect of Al/Ti molar ratio on the catalyst activity, polymerization was performed with **1ATiCl$_2$** at room temperature by varying the Al/Ti molar ratio from 100 to 500. When Al/Ti ratio was 100, catalyst activity was 0.14 kg of PH/mol-Ti·h (entry 1, Table 1). The catalyst showed improved activity (0.62 kg of PH/mol-Ti·h) when Al/Ti ratio was 300 with improved molecular weight (entry 2, Table 1). Further increase in Al/Ti ratio led to decrease in molecular weight with broadening of molecular weight distribution (Table 1). ^{1}H NMR of the obtained PH showed a more intense peaks in the region of 4.5 ppm at higher Al/Ti ratio suggesting that termination due to transfer to aluminum is predominant at higher Al/Ti ratio.

When the Al/Ti ratio was 100, isotacticity (percentage of *mmmm* pentad) was 72% and it increased to 85% for Al/Ti ratio of 500. In general it has been observed that % isotacticity increases with increase in Al/Ti ratio. This may be due to tight contact pair between active metal centre and MAO, which reduces the site isomerization [29]. Similar results have been observed for other two catalysts systems **2ATiCl$_2$** and **3ATiCl$_2$**/MAO.

When we used TMA depleted MAO(dry MAO) [30] the activity increased fivefold and also the resulting PH showed higher molecular weight with lower PDI values [31] possibly due to decrease in chain transfer reaction after the removal of TMA from MAO as revealed by ^{1}H and ^{13}C NMR of the obtained PH. In general, with TMA depleted MAO these precatalysts showed better activity at lower Al/Ti ratio when compared to commercial MAO.

Dibenzyl titanium complexes **1ATiBn$_2$** and **3ATiBn$_2$** were prepared by benzylation of the corresponding chloride analogs with BnMgBr (Scheme 2) as per literature procedure. Under identical conditions, these dibenzyl complexes upon activation with MAO or $Ph_3CB(C_6F_5)_4$ showed lower activities compared to chloride analogs. The resultant PH possessed lower molecular weights with narrow molecular weight distribution (Table 2). The isotacticity of the obtained polymers ranged from 87 to 90%. The lower activity of these benzylic complexes may be due to less thermal stability as compared with methyl cationic complexes [32].

3.5. Effect of temperature

To understand the effect of polymerization temperature on catalyst activity, PH molecular weight and PDI, we carried out 1-hexene polymerization at different temperatures (−10 to 50 °C) using **1ATiCl$_2$**/MAO system. The activity of **1ATiCl$_2$** increased when the polymerization temperature was increased from −10 to 35 °C. But the activity decreased on further increase in temperature (Table 1). At lower polymerization temperatures the produced polymers have higher molecular weight. The molecular weight of the polymer increased twofold from 195,000 at 50 °C to 403,600 when temperature was lowered to 35 °C and further to 8,78,000 (fourfold) when temperature was further reduced to −10 °C (Fig. 5). At −10 °C the polymer had PDI as low as 1.07. With increase in polymerization temperature the PDI gradually increased, at 50 °C the PH had PDI of 2.93 (Fig. 5). The decrease in molecular weight with broadening of molecular weight distribution at higher polymerization temperatures suggests a higher rate of chain transfer reactions. The decrease in activity at lower temperatures could be due to the slow activation of the

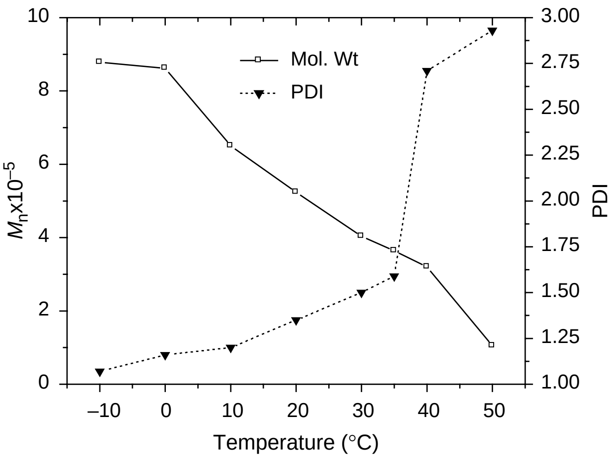


Fig. 5. Variation of molecular weight and PDI of PH with polymerization temperature for **1ATiCl$_2$**/MAO system.

precatalyst to generate the necessary active species. The percentage isotacticity increased with decrease in polymerization temperature (Table 1). At −10 °C, the PH has 90% isotacticity and its tacticity sharply fell to 60% at 50 °C. Elevated temperatures causes loosening of the contact pair of metal active site and MAO, which leads to more mis-insertion [33,34].

4. Conclusion

In conclusion, a series of titanium based non-metallocene precatalysts have been prepared from *N*-substituted β-amino alcohols. Upon activation with MAO, these titanium complexes polymerized 1-hexene in an isotactic manner. As Al/Ti ratio increased beyond 300, decrease in molecular weight with broadening of molecular weight distribution was observed due to chain transfer to aluminum, but the isotacticity of the PH increased. It has been noticed that phenyl substitution in the α-position to oxygen in ligand is essential for effective catalysis of 1-hexene polymerization. The catalyst activity and polymer properties depend on the steric features in the ortho position of the aniline moiety of the ligands. With an increase in the bulkiness around the metal center, precatalysts showed higher activity and better steric control with increasing molecular weights.

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