Propylene polymerization catalyzed by constrained geometry (cyclopentadienyl)phenoxytitanium catalysts

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Abstract

Propylene polymerization was performed using three constrained geometry catalysts: 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butyl-phenoxytitanium dichloride (**1**), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenoxytitanium dichloride (**2**), and 2-(tetramethylcyclopentadienyl)-6-phenylphenoxytitanium dichloride (**3**) with $Al(^iBu)_3/[Ph_3C]^+[B(PhF_5)]_4{}^-$ as co-catalyst. The substituent effect of the ligand and the effect of the Al/Ti molar ratio on the catalytic properties were investigated. The catalytic activity decreases in the order of **1 > 2 > 3**. The ^{13}C NMR results show that the polymers are basically atactic polypropylene with some 2,1-insertion and 1,3-enchainment units in the polymer chain, and the end groups are mainly vinylidene ($CH_2=CMe–$) and vinyl ($CH_2=CH–$) together with a small amount of propenyl ($CH_3CH=CH–$). A possible chain propagation and termination mechanism of the propylene polymerization was discussed.
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Keywords: Propylene polymerization; Polypropylene; Constrained geometry catalyst; Metallocene; Titanium complex

1. Introduction

Group 4 constrained geometry metallocene catalysts, which have an appended chelating heteroatom donor group on the cyclopentadienyl ligand have received extensive attention in recent years [1–3]. In particular the constrained geometry catalysts (CGC) with a pendant nitrogen donor on the cyclopentadienyl ligand, such as $Me_2Si-(\eta^5-Me_4C_5)(^tBuN)TiCl_2$, have been widely studied in industry and academic institutions [4–7]. On the other hand, a considerable number of catalysts with a pendant oxygen donor on the cyclopentadienyl ligand have also been reported [8–14]. However, most of catalysts of this type have not been studied in detail with respect to their catalytic properties [14]. We have recently reported on the synthesis and catalytic properties for ethylene polymerization of a series of new constrained geometry cyclopentadienyl-phenoxy titanium dichlorides [15,16]. Considering that different stereospecific polypropylenes have been obtained with the constrained geometry catalysts of the $Me_2Si-(\eta^5-Me_4C_5)(^tBuN)TiCl_2$ type

under different conditions [17–20], we recently studied the catalytic properties for propylene polymerization of our constrained geometry cyclopentadienyl-phenoxy titanium catalysts in detail. The obtained polymers are basically atactic polypropylene with a small amount of $–(CH_2)_n–$ ($n > 3$) chain units, which are in somewhat extent similar to an ethylene-propylene copolymer. In this paper, we wish to report the results of propylene polymerization catalyzed by three constrained geometry catalysts (Chart 1), 2-(tetramethylcyclopentadienyl)-4,6-di-*tert*-butylphenoxytitanium dichloride (**1**), 2-(tetramethylcyclopentadienyl)-6-*tert*-butylphenoxytitanium dichloride (**2**), and 2-(tetramethylcyclopentadienyl)-6-phenylphenoxytitanium dichloride (**3**) with $Al(^iBu)_3/[Ph_3C]^+[B(PhF_5)]_4{}^-$ as co-catalyst, as well as the characterization of the obtained polymer samples.

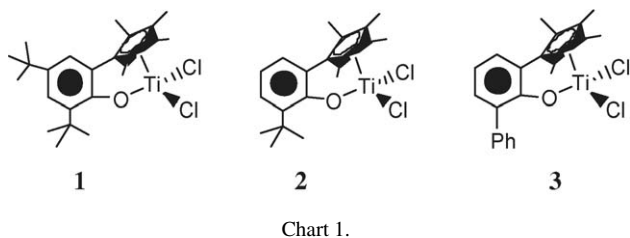## 2. Experimental

2.1. Materials

Complexes **1–3** [16] and $[Ph_3C]^+[B(PhF_5)]_4{}^-$ [21] were synthesized according to the literature procedure. $Al(^iBu)_3$, ^nBuLi

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Chart 1.

and $TiCl_4$ were purchased from Aldrich. Polymerization grade propylene (from Petro-China Company) was further purified by passage through a 5A molecular sieve column containing MnO. Solvents were dried and distilled prior to use [22]. NMR spectra were recorded on either a Varian Unity-400 or a Varian Mercury-300 NMR spectrometer.

2.2. Propylene polymerization

A dry 250 ml steel autoclave with a magnetic stirrer was charged with 80 ml of toluene, thermostated at desired temperature and saturated with propylene (1.0 bar). The polymerization reaction was started by injecting a mixture of catalyst and $Al(^iBu)_3$ in toluene (10 ml) and a solution of $[Ph_3C]^+[B(PhF_5)]_4^-$ in toluene (10 ml) at the same time. The vessel was repressurized to needed pressure with propylene immediately and the pressure was kept by continuously feeding propylene. After 30 min, the polymerization was quenched by injecting acidified methanol [HCl (3 M)/methanol = 1:1]. The mixture was stirred overnight and the polymer was collected by filtration, washed with water, methanol, and dried at 60 °C in vacuo to a constant weight.

2.3. Characterization

The compositions of the polymers were determined by ^1H NMR and ^{13}C NMR. The ^{13}C NMR experiments were performed in o-dichlorobenzene-d_4 at 120 °C with an acquisition time of 1 s, a pulse width of 90° and a delay time of 8 s.

3. Results and discussion

3.1. Propylene polymerization

Complexes **1–3** can all catalyze the polymerization of propylene to produce viscous oily polypropylene with lower molecular weight ($M_w = 1–2 \times 10^4$) upon activation with $Al(^iBu)_3/[Ph_3C]^+[B(PhF_5)]_4^-$. Fig. 1 shows the catalytic activity of **1–3** as a function of the Al/Ti ratio at polymerization temperature 70 °C. The order of catalytic activity is **1 > 2 > 3**, which could be attributed to the nature of the substituents on the phenolate. By comparing the catalytic activity of **1** and **2** or **2** and **3**, it can be clearly seen that the electronic effect of the substituent groups at both the para and ortho positions of the phenolate plays a significant role. For all complexes **1–3**, the catalytic activity increases with the increase in the Al/Ti ratio and reaches the
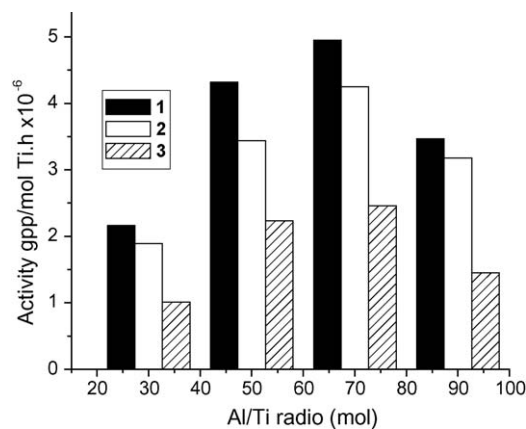

Fig. 1. The effect of Al/Ti ratio on the catalytic activity.

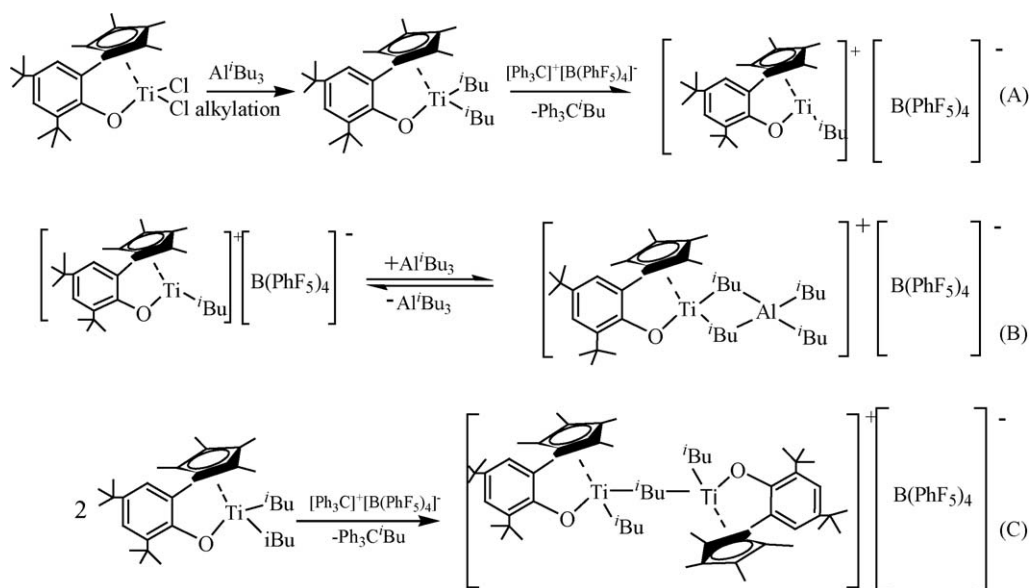Table 1
Results of polymerization catalyzed with **(1)–(3)**[a]

Catalyst	Run	T (°C)	Al/Ti (mol)	Complex[b] ($\times 10^{-6}$ mol)	Yields (g)	Activity ($\times 10^{-6}$ mol)[c]	M_w[d] ($\times 10^{-4}$)
1	1	70	30	2.26	2.44	2.16	1.8
	2	70	50	2.26	3.97	3.51	1.5
	3	70	70	2.26	5.59	4.95	1.7
	4	70	90	2.26	3.92	3.47	1.4
	5	50	70	2.26	2.11	1.87	2.4
2	6	70	30	2.58	2.44	1.89	1.7
	7	70	50	2.58	4.18	3.24	1.6
	8	70	70	2.58	5.48	4.25	1.6
	9	70	90	2.58	4.10	3.18	1.4
3	10	70	30	2.46	1.24	1.01	1.8
	11	70	50	2.46	2.74	2.23	1.6
	12	70	70	2.46	3.03	2.46	1.7
	13	70	90	2.46	1.78	1.45	1.5

[a] Condition: pressure = 0.3 MPa, reaction time = 0.5 h, B/Ti(mol) = 1.2, B = $[Ph_3C]^+[B(PhF_5)]_4^-$, toluene = 80 ml.
[b] Addition amount of complex.
[c] Activity, gpp/mol Ti h.
[d] Intrinsic viscosity measured at 135 °C in THN, M_w estimated from $[\eta] = 1.85 \times 10^{-4} M_w^{0.757}$.

Scheme 1. The formation and interrelation of different cationic species.

highest catalytic activities with the Al/Ti ratio of about 70. Further increasing in the Al/Ti ratio results in a decrease in the catalytic activity (also see Table 1). This behavior is similar to the results [23,24] observed for propylene polymerization with Cp_2ZrCl_2/MAO catalyst systems and can be easily explained. Impurities in the reaction system could not be effectively cleaned at lower Al/Ti ratios [25], while excessive $Al(^iBu)_3$ would consume so much $[Ph_3C]^+[B(PhF_5)]_4^-$ that the catalyst could not be efficiently activated. Moreover, it has been well documented in literature that different cationic species [26,27] with catalytic activity could be formed when metallocene catalysts are activated with $AlR_3/[Ph_3C]^+[B(PhF_5)]_4^-$.

Scheme 1 shows the formation and transformation of possible cationic species **A**–**C** in the present system. The formation of the less active cationic species **C** due to a shortage of $[Ph_3C]^+[B(PhF_5)]_4^-$ could further decrease the catalytic activity of the system. It is thus important to have enough $[Ph_3C]^+[B(PhF_5)]_4^-$ in the polymerization system. The formation of the heterobinuclear cationic adduct **B** might result in a decrease in the polymer molecular weight with the increase in the Al/Ti radio due to the polymer chain transfer from Ti to Al [28]. However, experimental results (Table 1) show that the polymer molecular weight does not change very much with the change of the Ai/Ti radio, which indicates that the chain transfer to Al is not remarkable in the present system and the chain termination mainly takes place *via* β-H elimination [29–31] or β-Me elimination [30–32] (see Fig. 2). It has been reported that the bulky Al-^{i}Bu unit shows little tendency to exchange with a Zr-polymer unit [33].

3.2. NMR analysis

The ^{1}H NMR spectra of two typical polypropylene samples from catalyst **1** are shown in Fig. 2. Both the resonances at 4.75 and 4.82 ppm caused by β-H elimination and the resonances at 4.94 and 5.16 ppm caused by β-Me elimination denote

hydrogen atoms in unsaturated double bonds on the polymer chain end. The major polypropylene end groups are vinylidene (CH_2=CMe–), resulting from β-H transfer following a 1,2-insertion, and vinyl (CH_2=C–), resulting from β-H transfer from the methyl group following a 2,1-insertion or from β-Me transfer following a 1,2-insertion. Small amounts of internal olefins are also formed *via* β-H transfer following a 2,1-insertion [20]. The indiscriminate nature of the propylene polymerization is owing to the open nature of these catalysts. Thereby, 2,1-insertion can take place more readily than in the cases using other metallocene catalysts.

The ^{13}C NMR spectra of the typical polypropylene samples from catalyst **1** are shown in Fig. 3. According to published literatures [34–39], the resonances for the carbons indicated in Scheme 2 can be assigned as shown in Fig. 3. The resonances observed in the region of methyl group (Fig. 4) are 22.1 ppm
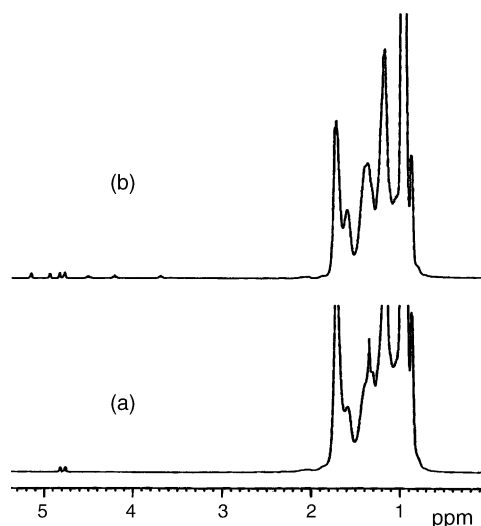

Fig. 2. ^{1}H NMR spectra of polypropylene samples obtained at: (a) 70 °C with Al/Ti = 70 and (b) 50 °C with Al/Ti = 70.
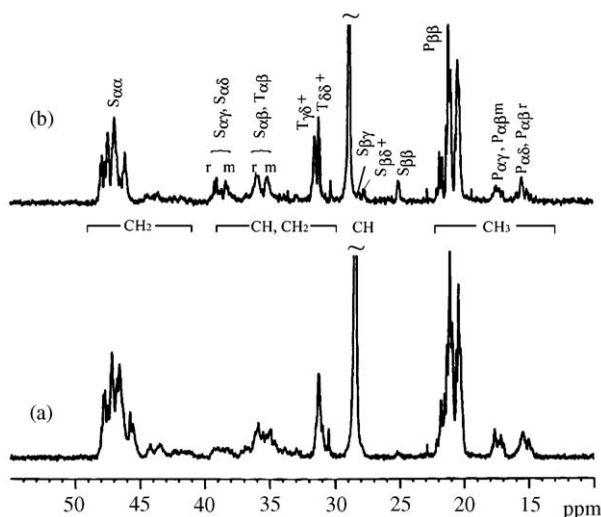
Fig. 3. ^{13}C NMR spectra of polypropylene samples obtained at: (a) 70 °C with Al/Ti = 70 (triads mm = 10.4%, mr = 58.1%, rr = 31.5%) and (b) 50 °C with Al/Ti = 70 (triads mm = 14.6%, mr = 53.7%, rr = 32.7%).

Fig. 4. The methyl region of the ^{13}C NMR spectrum (b) in Fig. 3.

for the pentad mmmm, 21.8 ppm for mmmr, 21.5 ppm for rmmr, 21.3 ppm for mmrr, 21.1 ppm for mmrm + rmrr, 20.9 ppm for mrmr, 20.6 ppm for rrrr, 20.4 ppm for rrmm, and 20.3 ppm for mrrm. The ratio of intensities of the resonances for rmmr, mmrr, and mrrr pentads is roughly 1:1.4:2.9 for the sample in Fig. 3a and 1:0.9:3.26 for the sample in Fig. 3b, which is in agreement with a slightly syndiotactic structure [40]. Methylene carbon resonances of $S_{\alpha\delta+}$ (38.9–39.2 ppm, $n = 4^+$), $S_{\alpha\gamma}$ (38.1–38.7 ppm, $n = 3$), $S_{\beta\gamma}$ (28.1 ppm, $n = 4$), $S_{\beta\delta+}$ (27.6–27.8 ppm, $n = 5^+$), and $S_{\beta\beta}$ (25.0–25.1 ppm, $n = 3$) can be found in Fig. 3b for the typical polypropylene sample produced at 70 °C, which is indicative of the existence of –$(CH_2)_n$– chain with $n = 3–5$ and the chain propagation with 2,1-insertion and 1,3-enchainment. The resonance signals of methine carbons found in 35.1–36.0 ppm region ($T_{\gamma\delta+}$, $T_{\delta\delta+}$) support the above structural features. Res-
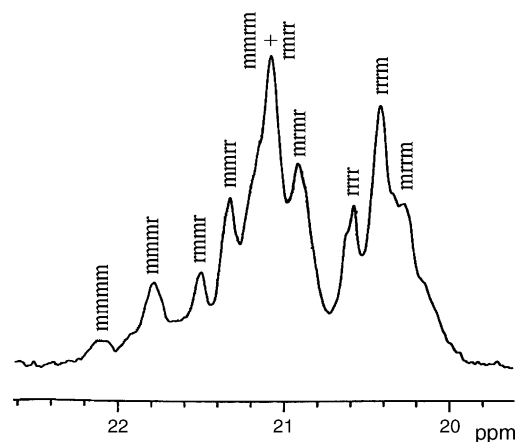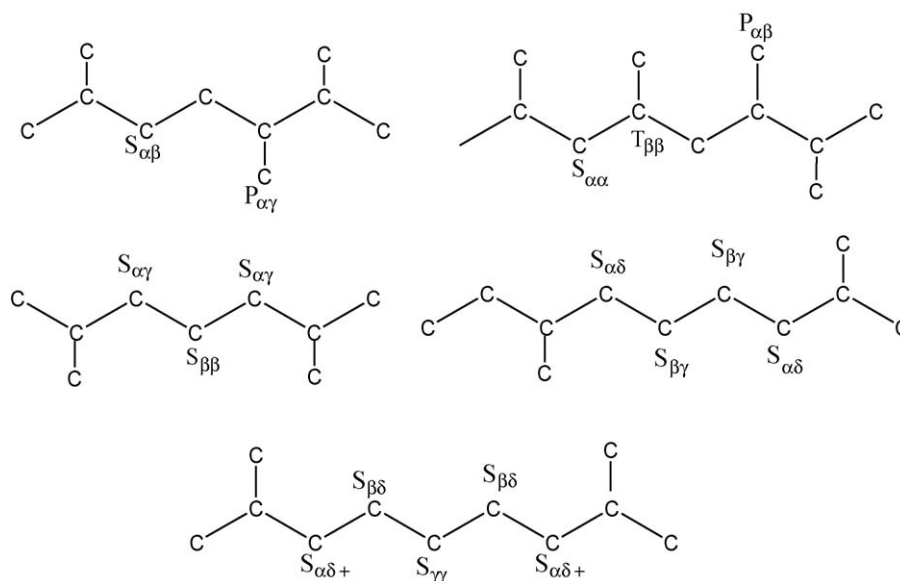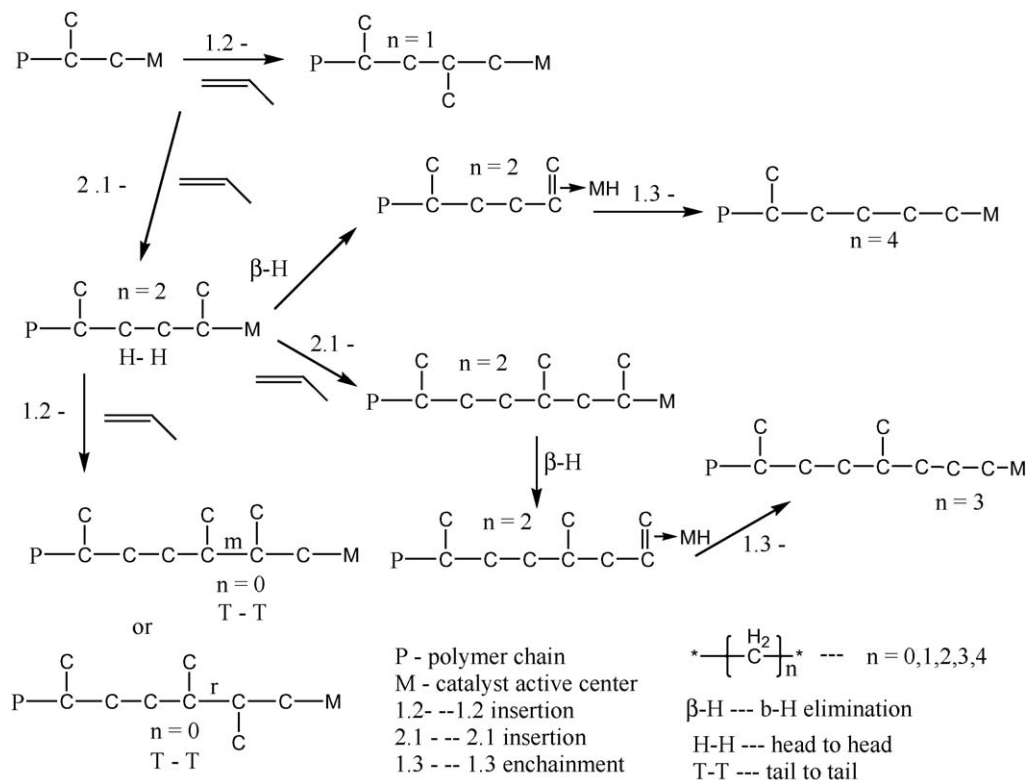
onances of adjacent methyls in tail-to-tail fragments are found in the 14–18 ppm region in Fig. 3, and the resonance from 14.7 to15.9 ppm and 17.0 to17.8 ppm can be assigned to $P_{\alpha\beta}$ and $P_{\alpha\gamma}$ with r and m stereochemistry, respectively. Based on above NMR analysis, a possible chain propagation mechanism as shown in Scheme 3 is proposed to explain the microstructure of the polypropylenes. The –$(CH_2)_n$– segments found in polypropylenes can be formed by a 2,1-insertion, a 1,3-enchainment, or their combination [39]. The existence of long –$(CH_2)_n$– segments indicates that the polypropylenes produced by these catalysts are somewhat similar to the ethylene-propylene (E/P) copolymers.

Dyad, triad and pentad distribution and statistical analysis for the polypropylenes were calculated and listed in Table 2. Triads% and rde% [41] values also indicate that the polypropylenes are slightly syndiotactic. The fact that 1,3-% values increase with the increase in reaction temperature indicates that the 2,1-insertion increases compared with 1,2-insertion at high temperatures.

Scheme 2. Typical microstructure segments of the obtained polypropylene.

P - polymer chain
M - catalyst active center
1.2- --1.2 insertion
2.1 - -- 2.1 insertion
1.3 - -- 1.3 enchainment

$*-[CH_2]_n-*$ --- n = 0,1,2,3,4

β-H --- b-H elimination
H-H --- head to head
T-T --- tail to tail

Scheme 3. A possible chain propagation process for the formation of polypropylene.

Table 2
Pentad, triad and dyad distribution and statistical analysis for polypropylenes

Catalyst	T (°C)	Triads%			Dyads%		%rde[a]	1,3-%[b]	Pentads%								
		mm	mr	rr	m	r			mmmm	mmmr	rmmr	mmrr	mmrm/rmrr	mrmr	rrrr	rrrm	mrrm
1	50	14.6	53.7	32.7	40.4	59.6	19.2	5.2	1.94	7.38	5.57	8.29	25.05	14.22	8.33	16.89	12.29
1	70	10.4	58.1	31.5	39.4	60.6	21.2	16.4	2.2	5.2	6.0	5.5	20.0	19.95	6.24	19.56	16.0

[a] %rde = %r − %m, a positive value is indicative of syndiospecificity, and a negative one is related to isospecificity.
[b] 1,3-% is the percentage of 2,1-insertion followed by isomerization to 1,3-enchainment, 1,3-% = $(100)(1000 - B)/(1000 + 2B)$, where B is the total methyl groups per 1000 methylene groups [38].

4. Conclusion

Upon activation with $(Al^iBu_3)/[Ph_3C]^+[B(PhF_5)_4]^-$, complexes **1**–**3** can catalyze propylene polymerization to produce basically atactic polypropylenes with lower molecular weight ($M_w = 1-2 \times 10^4$). The order of catalytic activity for propylene polymerization under similar conditions is **1 > 2 > 3**. ^{1}H NMR analysis indicates that the polymer chains are terminated with vinylidene and vinyl groups. ^{13}C NMR analysis indicates that the polypropylenes obtained are somewhat similar to an ethylene-propylene (E/P) copolymer with long $-(CH_2)_n-$ ($n \geq 2$) sequence units.

Acknowledgments

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