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ORIGINAL PAPER

Polymerization of ethylene to branched poly(ethylene)s using *ansa*-η^5-monofluorenyl cyclohexanolato zirconium(IV) complex/methylaluminoxane

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Abstract *ansa*-η^5-Monofluorenyl cyclohexanolato zirconium complex **3** was shown to be active for the polymerization of ethylene when activated with methylaluminoxane (MAO) at 5 bar. Up to a polymerization temperature of 40 °C, **3**/MAO resulted in linear poly(ethylene)s with saturated chain ends. However, at polymerization temperatures of 60, 80, and 100 °C, a mixture of branched poly(ethylene)s, linear α-olefins and long chain alkanes was obtained. The poly(ethylene)s produced at 80 and 100 °C exhibited a bimodal molecular weight distribution indicative of multiple active species. Very high molecular weight ($M_v > 5 \times 10^5$) linear poly(ethylene)s were obtained using **3**/MAO at 25 °C.

Keywords *ansa*-Monofluorenyl complex · Methyl aluminoxane · Ethylene polymerization · Branched poly(ethylene)s · Bimodal MWD

Introduction

There have been significant advances in the last two decades in the field of olefin polymerization by homogeneous early transition metal complexes. A considerable amount of research has been aimed at understanding how the catalyst structure correlates with the resulting polymer properties. Among these, early transition metal complexes with bidentate ligands that combine two anionic functions such as cyclopentadienyl, indenyl, or fluorenyl with built-in alkoxide or amide groups have attracted much attention as catalysts for the oligomerization or polymerization of olefins. Such ligands have not only led to the development of new single site catalysts but have also enabled control over stereoregularity, molecular weight, microstructure, comonomer incorporation and thermal/rheological characteristics

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[1–4]. Constrained geometry catalysts (CGC) that contain a cyclopentadienyl ring and amido ligand linked together with a dimethylsilyl bridge have been developed by Dow and Exxon. These complexes, due to their open structure, are capable of copolymerizing ethylene with α-olefins and also bulky monomers such as styrene [5–16]. There has also been increasing interest in constrained geometry catalyst systems which could produce branched polyethylene from pure ethylene feed. Miller et al. [17] reported a fluorenyl silyl amido zirconium complex that produces highly branched polyethylene from ethylene alone.

Another class of olefin polymerization catalysts is monocyclopentadienyl complexes with ancillary oxygen donors of the type CpM(OR)X. These types of complexes are of interest because of the ease of their synthesis and their similarity to the constrained geometry catalysts. A novel cyclopentadienyl phenolate titanium catalyst system active in the polymerization of olefins was reported by Marks and coworkers [18]. This complex when activated with $[Ph_3C]^+[B(C_6F_5)_4]^-$ exhibited high activity for polymerization of ethylene, propylene, and styrene producing high molecular weight ($>10^6$) poly(ethylene)s as well as atactic PP and PS. Mu and coworkers reported constrained geometry tetramethyl cyclopentadienyl phenoxy titanium complexes which when activated with $Al(^iBu)_3$ and $Ph_3C + B(C_6F_5)_4^-$ exhibited reasonable activity for ethylene polymerization, resulting in polyethylenes with moderate molecular weights [19]. Copolymerization of ethylene and hexene-1 at elevated temperature of 210 °C using silicon-bridged fluorenyl phenoxy Group IV metal complexes have been studied by Senda et al. [20], resulting in copolymers with high molecular weights and high hexene-1 content. Olefin polymerization catalysts based on half-metallocenes containing anionic ancillary donor ligands have been reviewed by Nomura et al. [21].

However, compared to monocyclopentadienyl aryloxy complexes, reports on monocyclopentadienyl alkoxy complexes of Group 4 metals are relatively scarce. Gielens et al. [22] reported a titanium hydrocarbyl complex with a linked Cp-alkoxide ancillary ligand which exhibited an activity of 263 g PP $mmol^{-1}$ Ti h^{-1} for polymerization of propylene. Poly(propylene)s formed were atactic with a noticeable amount of 2,1-misinsertions. The synthesis of zirconium complexes based on *trans*-2-[9-(H)-fluorenyl] cyclopentanol and cyclohexanol has been reported by Rieger [23]. However, their catalytic activities for olefin polymerization were not reported.

In this article, we report the synthesis of an *ansa*-fluorenyl cyclohexanolato zirconium complex (**3**) and its ability to produce branched polyethylene from ethylene alone. The presence of a metal–oxygen bond was expected to improve the thermal stability of the complex that may make them suitable for use at high temperatures. Complex **3** when activated with methylaluminoxane (MAO) resulted in branched poly(ethylene)s at higher temperatures along with significant amounts of low molecular weight oligomers. An interesting feature of this catalyst system was that the oligomers consist of long chain alkanes in addition to linear α-olefins. To the best of our knowledge, this is the first report of a carbon-bridged mono-fluorenyl alkoxy zirconium complex that produces long chain alkanes by ethylene oligomerization. A bis (phenoxyimine) zirconium complex has recently been reported to produce exclusively Al-terminated poly(ethylene)s by chain transfer to aluminum

[24]. An iron(II) bis(imino) pyridyl catalyst system was reported in the literature to afford a mixture of α-olefins and long chain alkanes by ethylene oligomerization [25]. The branched poly(ethylene)s produced by **3**/MAO was found to consist of mainly long chain branches and some methyl branches at higher temperatures.

Experimental section

General considerations

All manipulations of air- and/or moisture-sensitive compounds were performed using high vacuum or Schlenk techniques. High purity nitrogen or argon was used as the inert gas. Toluene and tetrahydrofuran were procured from S.D. Fine Chem Ltd., India and were purified by distillation over sodium/benzophenone. Fluorene (98%), *n*-Butyl lithium (2.5 M solution in hexane), and $ZrCl_4$ were procured from Aldrich. Epoxycyclohexane (synthesis grade) was obtained from Merck, India. Tetrahydrofuran and toluene were procured from S.D. Fine Chem. Ltd., India and were distilled over sodium/benzophenone prior to use. MAO was purchased from Witco GmbH, Germany as 30 wt% solution in toluene. Polymerization grade ethylene was obtained from gas cracker complex of Indian Petrochemical Corporation Limited, Nagothane, India. $ZrCl_4(thf)_2$ was prepared according to literature procedure.

Synthesis of *trans*-2-[9-(H)-fluorenyl] cyclohexanol (**2**)

Compound **2** was synthesized according to literature procedure [23]. An oven-dried 250 mL Schlenk flask was cooled under vacuum and charged with argon. Fluorene (2 g, 12 mmol) was taken in it and dissolved in dry diethyl ether. An ethereal solution of *n*-BuLi (5 mL, 12.5 mmol of 2.5 M solution in hexane) was added to this solution at 0 °C over a period of 45 min. It was stirred for 1 h and epoxycyclohexane (1.2 mL, 12 mmol) was added dropwise to it at 0 °C over a period of 1 h. The mixture was stirred at 25 °C for 12 h. The product was hydrolyzed with aqueous ammonium chloride solution. Ether layer was separated, dried over anhydrous sodium sulphate and concentrated to obtain **2** as a pale yellow solid. The compound was further purified by column chromatography. Yield: 2.70 g (85%); Analysis for $C_{19}H_{20}O$: Calcd., % C 86.34 H 7.63; Found, % C 86.25 H 7.52; ^{1}H-NMR ($CDCl_3$, 400 MHz): δ ppm 7.2–7.9(m, 8 H), 4.55(d, 1 H), 3.95(m, 1 H), 0.57–2.2(m, 10 H); ^{13}C-NMR ($CDCl_3$, 100 MHz): δ ppm 24.47, 24.84, 25.32, 36.49, 47.30, 49.65, 72.22, 119.35, 119.68, 123.76, 125.48, 126.40, 126.59, 126.77, 141.40, 141.66, 145.08, 147.06.

Synthesis of *ansa*-(η^5-fluorenyl cyclohexanolato) bis(tetrahydrofuran) zirconium(IV) dichloride (**3**)

The following literature procedure was adapted for the synthesis of complex **3** [23]. In an oven-dried 250 mL Schlenk flask, cooled under vacuum and charged with argon was taken compound **2**(0.264 g, 1 mmol) and dissolved in THF. *n*-BuLi (0.8 mL, 2 mmol) was added to it at 0 °C slowly and stirred for 30 min. The flask was cooled to −78 °C and $ZrCl_4$ $(thf)_2$ (0.377 g, 1 mmol) dissolved in THF was added dropwise. The reaction mixture was refluxed for 6 h. THF was evaporated, dichloromethane was added and the solution filtered through a Celite bed to remove LiCl. Dichloromethane solution on evaporation gave a yellow solid, which was washed with hexane and dried in vacuum. Elemental analysis of the complex showed the presence of 2 THF molecules coordinated to the metal center. Yield: 0.38 g (67%); Analysis for $C_{19}H_{18}OZrCl_2$ 2 C_4H_8O: Calcd., % C 57.02 H 5.98; Found, % C 56.76 H 6.06; ^{1}H-NMR (C_6D_6, 400 MHz): δ ppm 0.8–1.6 (cyclohexyl 8H), 1.4 (THF, C**H**$_2$–CH$_2$–O, 8H) 2.8 (cyclohexyl, C**H**-fluorenyl, 1H), 3.5 (THF, CH$_2$–C**H**$_2$–O, 8H), 4.7 (cyclohexyl, C**H**–O, 1H), 7.2–7.8 (aromatic, 8H).

Polymerization of ethylene

Polymerization of ethylene was performed at 5 bar pressure in a Buchi AG miniclave. The oven-dried glass reactor was cooled in an atmosphere of ethylene. Toluene (30 mL) was injected into the reactor through a hypodermic syringe and stirred for 10 min in order to achieve saturation with ethylene. Cocatalyst was introduced into the reactor through a syringe. Finally, the catalyst solution was added through a syringe and the reactor was pressurized with ethylene. After 60 min, polymerization was terminated by addition of methanol containing 15% dilute hydrochloric acid and the polymer was precipitated in methanol. The polymer was filtered, washed several times with methanol, and dried at 60 °C in vacuum.

Characterizations

^{1}H and ^{13}C-NMR spectra of the ligands were recorded in $CDCl_3$ on a 400 MHz Bruker NMR spectrometer. Elemental analysis was performed on a CHNS-O EA 108 Elemental analyzer. DSC of the homo- and copolymers were recorded on a Perkin Elmer DSC 7 instrument. The sample was initially heated up to 150 °C at a heating rate of 10 °C/min and then rapidly cooled to 50 °C at a rate of 100 °C/min. Finally, the sample was again heated at a rate of 10 °C/min. The melting points reported were calculated from the second heating curve. Quantitative ^{13}C-NMR of the polymers were recorded on Bruker DRX-500 NMR spectrometer at 130 °C under quantitative conditions (90° pulse followed by 10 s delay). Samples were prepared by dissolving about 200 mg of the polymer in 2 mL of 1,2-dichlorobenzene/benzene-d_6 or 1,1,2,2-tetrachloroethane-d_2 in a 10-mm-o.d. tube. Molecular weights and molecular weight distributions of the polymer samples were determined by high temperature GPC analysis. A GPC instrument, PL 220, equipped with a refractive index detector was employed using μ-styragel columns (10^6, 10^5, 10^4, 10^3, 500 Å) and 1,2,4-trichlorobenzene as the solvent at 160 °C with a flow rate of 1 mL/min. Universal calibration method was used for analysis. The solvent was filtered through 0.45 μ membrane filter (Millipore) thrice prior to use. Polyethylene samples obtained at polymerization temperatures of 25 and 40 °C could not be analyzed by GPC in view of the high viscosities of their solutions.

Hence the molecular weights and molecular weight distributions of a few lower molecular weight samples are reported in this article.

Determination of the degree of branching in the polymer

The amount of long chain branching was calculated with respect to the signal at 34.57 ppm since the peak at 14.07 ppm (corresponding to methyl resonance) includes contribution also from saturated chain ends. Signal at 20.04 ppm is due to exclusively methyl branch and hence amount of methyl branches was calculated with respect to this signal.

Amount of branching in these poly(ethylene) samples was calculated by the following method:

No. of methyl branches, N_{M} = Integral value of the peak at 20.04 ppm
No. of long chain branches, N_{L} = Integral value of the peak at 34.57 ppm
Percentage of methyl branches with respect to total branching $= N_{\mathrm{M}}/(N_{\mathrm{M}} + N_{\mathrm{L}}) \times 100$
Percentage of long chain branches with respect to total branching $= N_{\mathrm{L}}/(N_{\mathrm{M}} + N_{\mathrm{L}}) \times 100$

Degree of branching was calculated by dividing the integral value of area for a single branch point by the total integral value of area for all the peaks and multiplying by 1000.

Relative percentage of alkanes with respect to α-olefins was calculated by using the following relationship [25]:

Intensity corresponding to one proton of α-olefin, $I_{\mathrm{H}\ \alpha\text{-olefin}} = (I_3/2 + I_4/2 + I_5)/3$
Intensity corresponding to one proton of alkane, $I_{\mathrm{H\ alkane}} = (I_1 - 3I_{\mathrm{H}\ \alpha\text{-olefin}})/6$

where I corresponds to the intensity of the peak and the subscript refers to the peak number in Table 6.

$$\%\ \text{of alkane} = I_{\mathrm{H\,alkane}}/(I_{\mathrm{H\,alkane}} + I_{\mathrm{H}\,\alpha-\mathrm{olefin}}) \times 100$$

Number average molecular weight (M_n) of the oligomers was determined from ^{1}H-NMR using the following procedure:

The integral corresponding to total protons is given by

$$I_{\mathrm{Total\ H}} = I_2 + 8I_{\mathrm{H}\,\alpha-\mathrm{olefin}} + 6I_{\mathrm{H\ alkane}}$$

I_2 is the integral that corresponds to the total methylene protons of the α-olefin and the alkane.

$$\text{Total number of protons in the oligomer} = I_{\mathrm{Total\ H}}/\left(I_{\mathrm{H}\,\alpha-\mathrm{olefin}} + I_{\mathrm{H\,alkane}}\right)$$

M_n can be determined from the product of the number of CH_2 present and the mass of CH_2 (14 g). The number of methylene units can be obtained by dividing the total number of protons by 2.

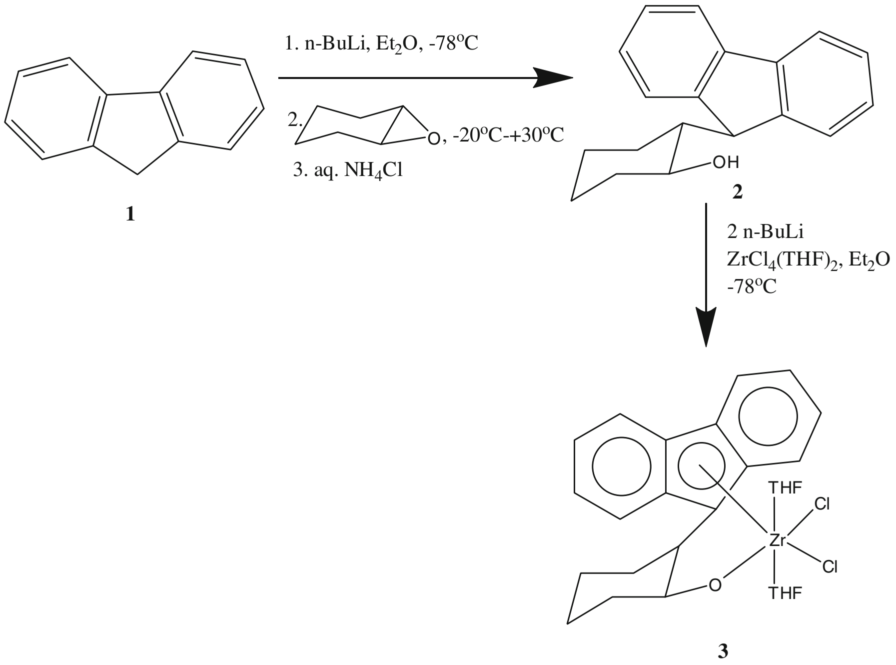
$$M_n\ \text{of oligomer} = (I_{\mathrm{Total\ H}}/I_{\mathrm{H}\,\alpha-\mathrm{olefin}} + I_{\mathrm{H\,alkane}})/2 \times 14$$

Results and discussion

Preparation and characterization of the ligand and zirconium complex **3**

Trans-2-[9-(H)-fluorenyl] cyclohexanol (**2**) and its zirconium complex were synthesized using the literature procedure (Scheme 1) and characterized by NMR spectroscopy and elemental analysis.

As reported by Rieger [23], elemental analysis and NMR spectrum showed the presence of two THF molecules coordinated to the metal center in complex **3**. In the ^{1}H-NMR spectrum, there are peaks corresponding to the cyclohexyl protons in the region 0.8–1.6 ppm and the aromatic protons in the region 7.2–7.8 ppm. Peaks at 1.4 and 3.5 ppm correspond to protons from THF molecules. There are two characteristic peaks at 2.8 and 4.7 ppm assigned to the cyclohexyl protons on carbon atoms adjacent to the fluorenyl group and oxygen atom, respectively. The presence of coordinated donor molecules in a metal complex is determined by steric and electronic factors around the metal center. Fluorenyl-based complexes are known to be more prone to donor molecule coordination than cylcopentadienyl and indenyl based systems as the metal center is more electrophilic due to delocalization of π electrons over two aromatic rings. Presence of fluorenyl ligand and more open nature of the complex **3** may be responsible for the presence of THF molecules in the coordination sphere of the complex. In spite of many attempts, single crystals of **3** suitable for XRD could not be obtained.



Scheme 1 Synthesis of *trans*-2-[9-(H)-fluorenyl] cyclohexanol and the zirconium complex

Polymerization of ethylene

Polymerization of ethylene was carried out using complex **3** and MAO as cocatalyst. The system was inactive for polymerization at 1 bar pressure. However, at 5 bar, **3**/MAO exhibited moderate catalyst activity. From Table 1 the following three observations can be made. First, catalyst activity was higher at higher ethylene pressures. This can be attributed to higher concentration of ethylene that effectively increases the polymerization rate. Second, higher catalyst activity was observed at higher temperatures. This could be ascribed to the loss of coordinated THF molecules from the metal center at temperatures above 60 °C [26]. Finally, presence of TMA enhanced the catalyst activity. TMA is capable of forming a stronger complex with THF, thus removing the THF from the coordination sphere of the metal [27].

Effect of temperature

Polymerization of ethylene was conducted using **3**/MAO in the temperature range 25–100 °C. Catalyst activity increased upon increasing the temperature from 25 to 60 °C and thereafter it decreased, probably due to deactivation of the active species (Table 2).

During isolation of the polymer, it was observed that the polymer obtained at temperatures 60, 80, and 100 °C was sticky in nature. Therefore, the following procedure was adapted for the purification of the polymer. The solid obtained after filtration was washed with boiling acetone to yield a solid polymer (hereafter designated as Fraction A). The acetone solution upon evaporation resulted in a waxy material (hereafter designated as Fraction B). The toluene-methanol layer (after precipitation and filtration of the solid) was neutralized with aqueous sodium bicarbonate solution, organic layer separated and concentrated to obtain liquid

Table 1 Polymerization of ethylene using **3**/MAO

Entry	Al/Zr	T_p (°C)	Activity[a]	$[\eta]^b$ dL/g	T_m (°C)
1	500	25	51	6.55	132
2	1,000	25	55	6.30	132
3	2,000	25	57	5.13	130
4	500	80	142	1.25	127
5	1,000	80	159	1.35	122
6	2,000	80	210	0.93	122
7[c]	1,000	25	63	6.18	135
8[d]	1,000	25	97	4.93	133

Toluene (30 mL); **3**: 17.6 μmol; $P_{ethylene}$: 5 bar; time: 1 h

[a] Expressed as g PE $mmol^{-1}$ Zr h^{-1}

[b] Measured in decahydronaphthalene at 135 °C

[c] **3** treated with 250 eqv of TMA for 10 min in the polymerization reactor before addition of MAO

[d] **3** pretreated with 250 eqv of TMA for 30 min before introducing into the polymerization reactor

Table 2 Effect of temperature on polymerization of ethylene using **3**/MAO

Entry	T_p (°C)	Total yield (g)	Acetone insoluble fraction (Fraction A) (g)	Acetone soluble fraction (Fraction B) (g)	Toluene soluble fraction (Fraction C) (g)	Activity g PE mmol^{-1} Zr h^{-1}
1	25	1.0	1.0	Nil	Nil	57
2	40	0.96	0.96	Nil	Nil	55
3	60	3.9	1.9	1.1	0.9	222
4	80	3.7	1.8	1.1	0.8	210
5	100	2.8	1.7	0.5	0.6	159

Toluene (30 mL); Zr: 17.6 μmol; MAO; Al/Zr: 2000; $P_{C_2H_4}$: 5 bar; time: 1 h

oligomers (hereafter designated as Fraction C). Thus, a mixture of insoluble solid polymer and soluble oligomers was obtained using the catalyst system **3**/MAO at 60, 80, and 100 °C. All the three fractions were separately characterized by thermal analysis and NMR spectroscopy.

Intrinsic viscosities and melting points of Fraction A obtained using **3**/MAO is shown in Table 3. A gradual decrease in molecular weights and melting points was observed upon increasing the polymerization temperature. DSC thermograms of Fraction A produced at different polymerization temperatures are shown in Fig. 1. GPC of poly(ethylene)s showed broad bimodal molecular weight distributions for Fraction A produced at 80 and 100 °C (Fig. 2).

Presence of branching in Fraction A was analyzed by means of ^{13}C-NMR spectroscopy. Nomenclature of Usami and Takayama for isolated branches [28] was used in order to make the carbon assignments for the branches (Fig. 3). Chemical shifts and assignments for branched poly(ethylene)s are given in Table 4. ^{13}C-NMR spectra of Fraction A produced at 25 and 40 °C showed peaks at 13.90, 22.77, 32.11, and 29.94 ppm corresponding to 1s, 2s, 3s, and main chain carbon atoms, respectively. Figure 4 shows the ^{13}C-NMR spectrum (in C_6D_6-ODCB) of Fraction A obtained at 25 °C. It can be noted that peak at 38.19 ppm characteristic of branched carbon was absent in the spectrum. Moreover, there are no peaks at 114.4 and 139.5 ppm due to unsaturated end group. This indicates that poly(ethylene)s consisted of only saturated chain ends resulting from chain transfer to aluminum alkyl.

^{13}C-NMR spectra of Fraction A obtained at 80 and 100 °C are shown in Fig. 5. The presence of a resonance signal at 38.19 ppm indicates that these polymers are branched. There are also peaks at 14.07, 22.80, 32.13, 29.40, 34.57, 27.25, and

Table 3 Characterization of Fraction A obtained with **3**/MAO

Entry	T_p (°C)	$[\eta]^a$ dL/g	M_w ($\times 10^4$)	M_w/M_n	T_m (°C)
1	25	5.1	n.d	n.d	132
2	40	4.7	n.d	n.d	130
3	60	1.04	n.d	n.d	125
4	80	0.93	12.2	Bimodal	121
5	100	0.59	7.7	Bimodal	123

[a] Measured in decahydronaphthalene at 135 °C

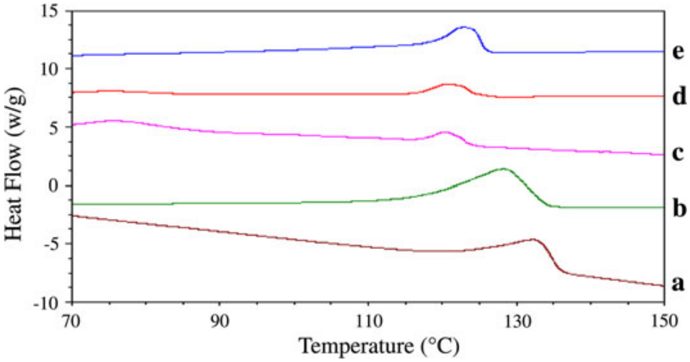


Fig. 1 DSC thermograms of Fraction A produced with catalyst **3**/MAO at different temperatures (*a*) entry 1, (*b*) entry 2, (*c*) entry 3, (*d*) entry 4, (*e*) entry 5 in Table 3

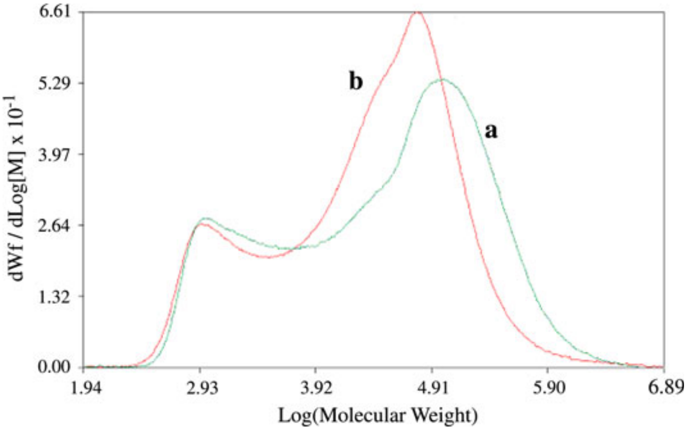


Fig. 2 GPC of Fraction A produced by **3**/MAO (*a*) entry 4, (*b*) entry 5, Table 3

30.48 ppm characteristic of long chain branching. These long chain branches may be formed as a result of in situ oligomerization of ethylene to α-olefins bearing long carbon chains and the reincorporation of these macromonomers into the growing polyethylene chains. The incorporation of macromonomers is presumably facilitated by the more open nature of complex **3**. Such a mechanism for long chain branching has been reported for constrained geometry catalysts [17].

It is interesting to note the appearance of peaks at 20.04 and 37.47 ppm in addition to the peaks due to long chain branches in the ^{13}C-NMR spectrum of Fraction A at 100 °C. These peaks can be ascribed to the presence of methyl branches, that may result from β-H elimination followed by 2,1-insertion of the α-olefin into the [Zr–H] species (Scheme 2). Appearance of these signals at higher temperatures indicates that the rate of 2,1-insertion increases with temperature. A similar observation has been reported for poly(ethylene)s obtained using pentamethylcyclopentadienyl tribenzyloxy titanium complex [29].

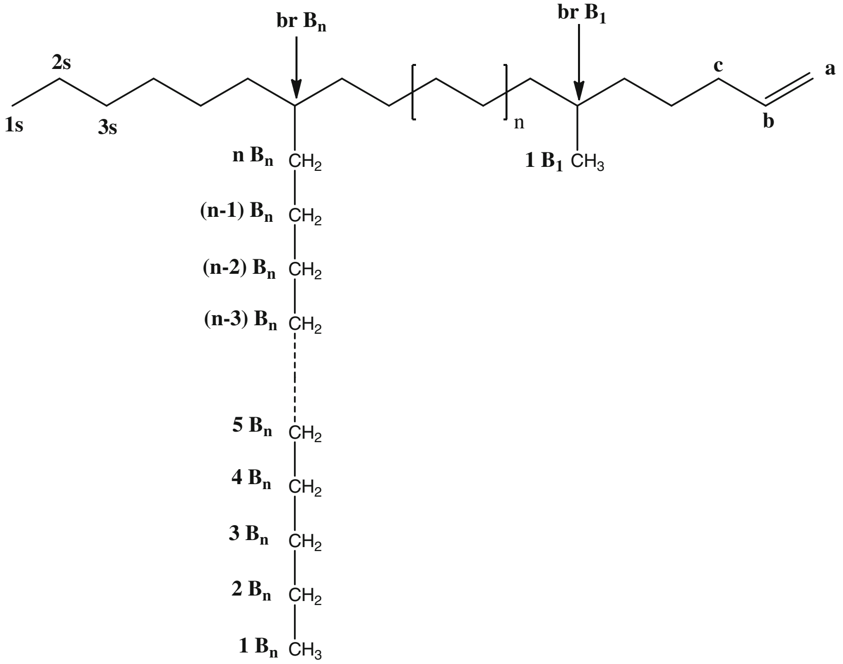


Fig. 3 Nomenclature for branched poly(ethylene)s (as per Ref. [28])

Amount of long chain branching was calculated with respect to the signal at 34.57 ppm since the peak at 14.07 ppm (corresponding to methyl resonance) includes contribution also from saturated chain ends. Signal at 20.04 ppm is due to exclusively methyl branch and hence amount of methyl branches was calculated with respect to this signal.

Degree of branching was calculated by dividing the integral value of area for a single branch point by the total integral value of area for all the peaks and multiplying by 1000. The results are summarized in Table 5.

Bimodal molecular weight distributions of poly(ethylene)s obtained using **3**/MAO at higher temperatures may be due to the presence of multiple active centres, one of which initiates the polymerization of ethylene to branched poly(ethylene)s and the other centre is capable of only oligomerizing ethylene to a mixture of linear α-olefins and long chain alkanes.

Typical ^{1}H and ^{13}C-NMR spectra of Fraction B are shown in Figs. 6 and 7. The spectra showed peaks due to the presence of linear α-olefins which are formed as a result of β-H transfer reactions (Table 6). In addition to this, there are also peaks due to saturated chain ends as seen from ^{13}C-NMR spectrum (peaks at 14.14, 22.85, and 32.15 ppm). The formation of these long chain alkanes can be explained as a result of chain transfer to aluminum.

Relative percentage of alkanes with respect to α-olefins was calculated by using the literature procedure [25] and the results are shown in Table 7.

Table 4 ^{13}C chemical shifts and assignments for branched poly(ethylene)s

Peak No.	Chemical shift exptl (ppm) in		Assignment
	1,1,2,2-tetrachloroethane-d_2	1,2-dichlorobenzene/benzene-d_6	
1	14.07	13.90	1Bn + 1s
2	20.04	19.87	1B1
3	22.80	22.74	2Bn + 2s
4	26.82		Unassigned
5	27.25	27.27	βBn
6	27.36	27.42	βB_1
7	29.90	29.90	$\delta\delta CH_2$ (main chain)
8	30.40		γB_1
9	32.13	32.07	3Bn + 3s
10	33.22	33.19	brB_1
11	33.92		$\mathbf{CH_2}$–$CH=CH_2$
12	34.57	34.54	αBn, nBn
13	37.47	37.48	αB1
14	38.19	38.19	brBn, brB1
15	38.90		Unassigned
16	114.4	114.4	$CH = \mathbf{CH_2}$
17	139.5	139.5	$\mathbf{CH} = CH_2$

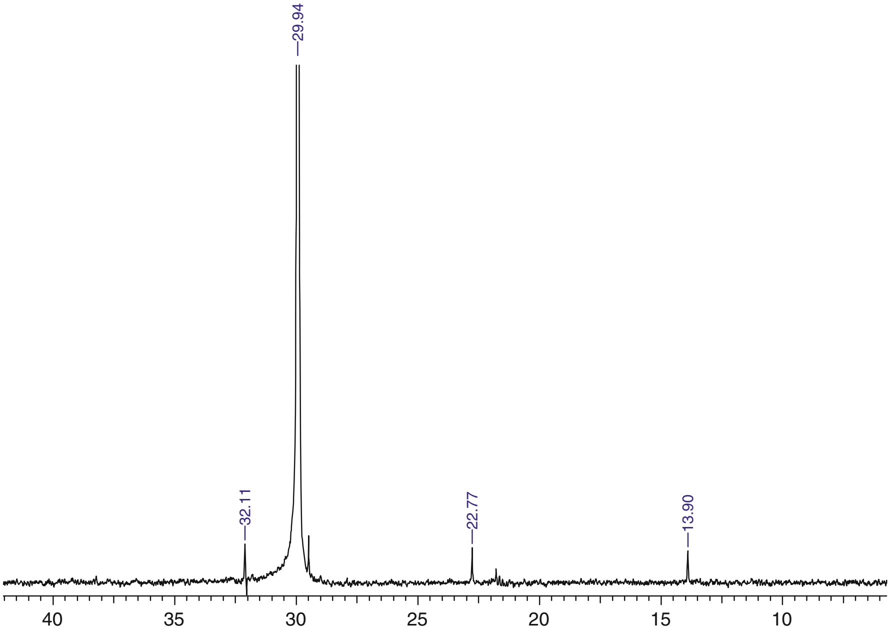


Fig. 4 Quantitative ^{13}C-NMR spectrum (in ODCB/C_6D_6) of Fraction A obtained from **3**/MAO at 25 °C

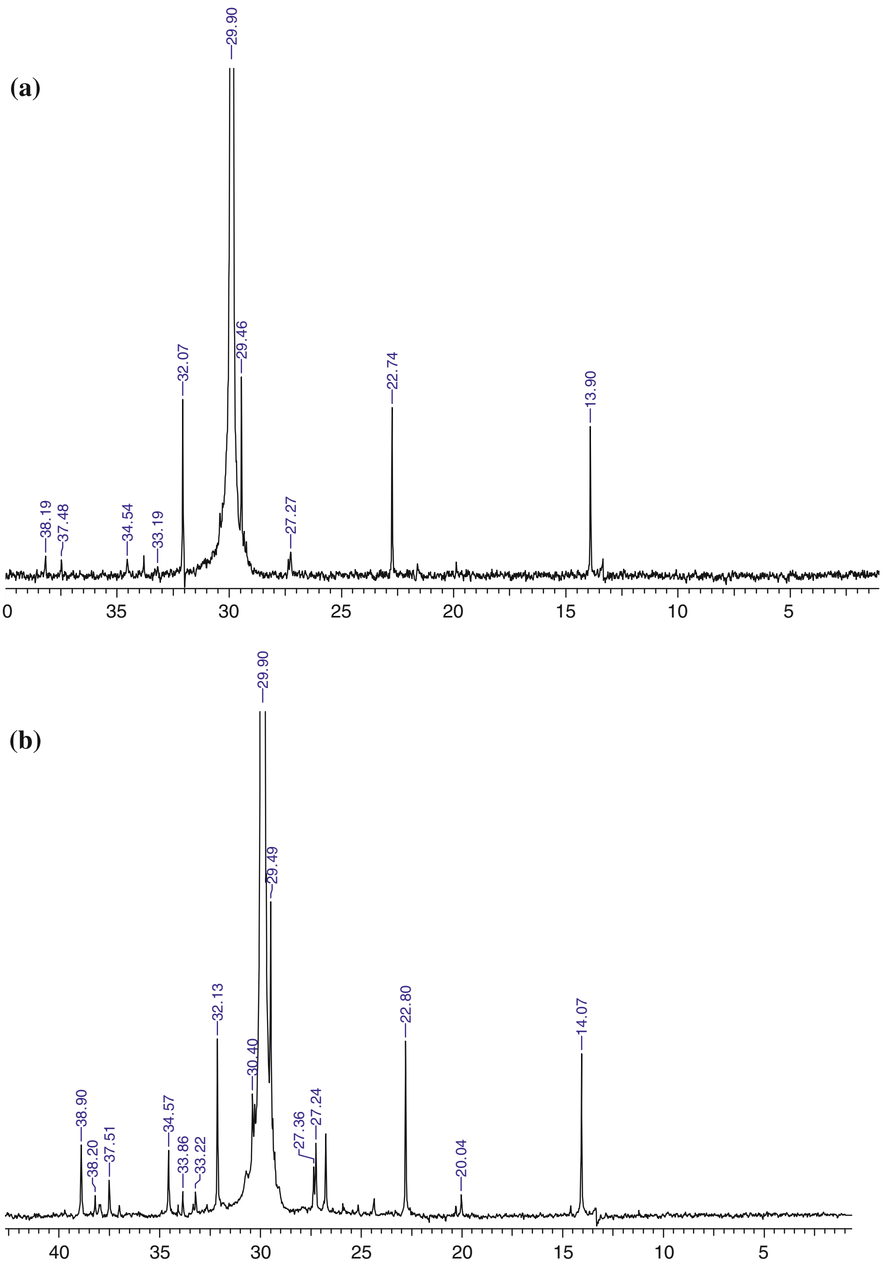
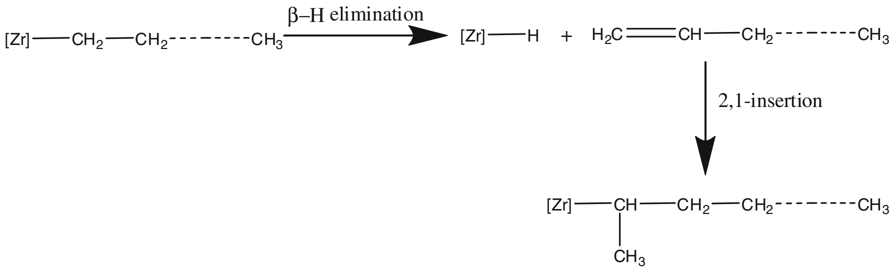


Fig. 5 Quantitative ^{13}C-NMR spectrum of Fraction A obtained from **3**/MAO at **a** 80 °C in ODCB/C_6D_6 and **b** 100 °C in $C_2D_2Cl_4$

Thus, Fractions B and C are low molecular weight oligomers (DP ~ 10), comprising a mixture of *n*-alkanes and α-olefins. The oligomers were rich in long chain alkanes (50–78%) which implies that chain transfer to aluminum is dominant.



Scheme 2 Mechanism for the formation of methyl branches

Table 5 Nature of branching and branching distribution of Fraction A obtained using **3**/MAO

Temperature	Total branching/ 1,000 °C	Branching with respect to total	
		Methyl (%)	Long chain (%)
25	0	0	0
40	0	0	0
60	0.5	0	100
80	1.4	0	100
100	2.6	60	40

As the temperature increased from 60 to 100 °C, α-olefin content in the oligomers increased from 22 to 50% (Table 7). This implies that the rate of β-H transfer becomes competitive with chain transfer to aluminum at higher temperatures. There are no peaks corresponding to branched carbon in the ^{13}C-NMR spectrum indicating that the oligomers are linear in nature. Presence of peaks at 4.91–5.04 ppm and 5.81–5.84 ppm in ^{1}H-NMR spectra also confirms the presence of vinyl end groups in these oligomers.

Conclusions

ansa-η^5-Monofluorenyl cyclohexanolato zirconium complex **3** was shown to be active for the polymerization of ethylene when activated with MAO at 5 bar pressure. **3**/MAO exhibited catalyst activity even at 100 °C. The thermal stability of the catalyst system can be attributed to the metal–oxygen bond in the complex **3**. When polymerization was conducted at 25 and 40 °C, the catalyst system resulted in linear poly(ethylene)s with saturated chain ends. This was attributed to chain transfer to aluminum operating at these temperatures. However, at 60, 80, and 100 °C, a mixture of insoluble solid polymer and soluble liquid oligomers was obtained. The solid poly(ethylene)s consisted of exclusively long chain branches (>6 carbons) at 60 and 80 °C, whereas, at 100 °C, methyl branches were observed in addition to the long chain branches. Long chain branches may be formed as a result of β-H transfer reaction followed by reincorporation of the resulting

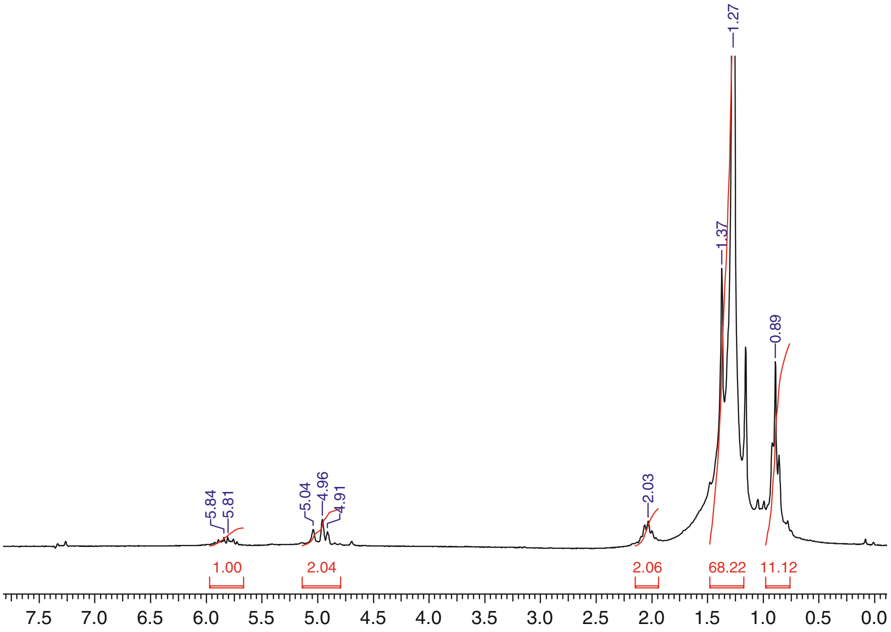


Fig. 6 ^{1}H-NMR spectrum (in $CDCl_3$, 200 MHz) of Fraction B obtained by **3**/MAO at 100 °C

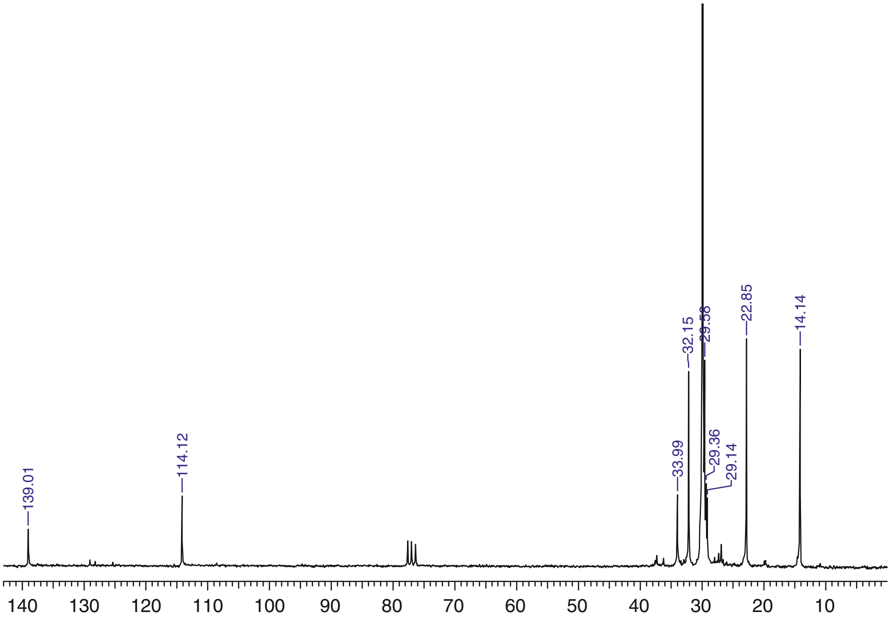


Fig. 7 ^{13}C-NMR spectrum (in $CDCl_3$, 50 MHz) of Fraction B obtained by **3**/MAO at 100 °C

Table 6 ^{1}H-NMR chemical shifts and their assignments for Fractions B and C

Peak No.	Chemical shift (ppm)	Assignments
1	0.89	$-\mathbf{CH}_3$
2	1.27–1.37	$-(\mathbf{CH}_2-)_n$
3	2.04	$-\mathbf{CH}_2-CH{=}CH_2$
4	4.91–5.06	$-\mathbf{CH}_2{=}CH$
5	5.70–5.78	$-CH_2{=}\mathbf{CH}-$

Table 7 Characterization of Fractions B and C obtained using **3**/MAO

T_p (°C)	% Alkanes[a]		M_n	
	Fraction B	Fraction C	Fraction B	Fraction C
60	76	78	320	300
80	69	61	310	250
100	50	57	280	200

[a] Balance α-olefins

macromonomers of ethylene into the growing polymer chains. The methyl branches result from *β*-H elimination followed by 2,1-insertion of the α-olefin into the [Zr]-H species. The soluble oligomer was found to be a mixture of linear α-olefins and long chain alkanes. Presence of long chain alkanes in the soluble fractions can be attributed to chain transfer to aluminum. Bimodal molecular weight distribution of poly(ethylene)s were observed when polymerization was conducted at 80 and 100 °C. This can be attributed to the presence of more than one active species, one capable of selective oligomerization and others capable of either homopolymerization or copolymerization of ethylene with higher α-olefins. In conclusion, complex **3**/MAO exhibits diverse polymerization behavior depending on temperature. High molecular weight, linear poly(ethylene)s, poly(ethylene)s with long chain branching or long chain, and short chain end branching could be obtained. To the best of our knowledge this is the first example of a fluorenyl alkoxy zirconium complex that exhibits such diverse polymerization behavior.

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