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Synthesis of low molecular weight polyethylene waxes by a titanium BINOLate–ethylaluminum sesquichloride catalyst system

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Abstract

Homogeneous complexes of Ti (IV) bearing sterically hindered bidentate diols such as 1,1′-binaphthalene 2,2′ diol (Binol) and substituted Binol were prepared and characterized. These catalyst precursors formulated as $[Ti(O\hat{}O)_2]$ or $[Ti(O\hat{}O)X_2]$ are found to be active in polymerization of ethylene at high temperatures in combination with alkyl aluminum sesquichloride ($Et_3Al_2Cl_3$) as co-catalyst. The polyethylenes obtained are linear, crystalline and display narrow polydispersities. The unique low molecular weight PE waxes formed in this reaction exhibit properties that have potential applications in surface coating and ink formulations. The influence of various reaction conditions on polymerization is discussed.
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Keywords: Titanium-binolate catalysts; Ethylaluminum sesquichloride; Polyethylene wax; Ethylene polymerization

1. Introduction

The design and development of well-defined homogeneous catalysts for the polymerization of ethylene constitutes a major area of research [1]. A potentially growing segment of global polyethylene business involves the production of specialty low molecular weight polyethylene waxes which are gaining importance for many applications. Industrially PE waxes can be obtained either through Fischer-Tropsch route or by polymerization of ethylene under controlled conditions using typical catalysts employed for high or low density polyethylene processes. Because of their unique physicochemical properties, commercial PE waxes find applications in enhancing lubricity, flow-modification, mold-release and anti-block properties in plastics processing. In addition they impart excellent slip and rub resistance in printing inks as well as in controlling set/softening point of hot-melt coatings and adhesives. For most synthetic waxes the required weight average molecular weights are generally below 3000 and the mean particle size around 10 μm [2]. The precise control of molecular weight of polyethylene having narrow polydispersity is primarily dependent on the nature of the catalyst as well as the reaction conditions. Currently major wax producers like Clariant and Dow (*Insite* catalyst) utilize proprietary metallocene catalysts and methylalumoxane as co-catalyst to manufacture highly crystalline, linear polyethylenes with lower molecular weights [3,4]. On the other hand Zeigler catalysts yield polyethylene with broad molecular weight distribution. Therefore, it was thought worthwhile to design suitable non-metallocene homogenous catalysts that are simple to prepare and less sensitive to moisture for polymerizing ethylene to wax grade polymer with desired molecular characteristics.

Though several new families of non-Cp based catalytic precursors have been explored in polymerization since early nineties they mainly lead to high molecular weight polyethylenes [5–7]. The most notable being late transition metal complexes of tridentate 2,6 diacetyl pyridylimine Schiff-base ligands and similar bidentate O^N bis-imine complexes of Ti(IV), Zr(IV) and Ni(II) [8–10]. There is, however, little attention paid to ligand systems involving bulky aryloxides and its complexes with group 4 metals in ethylene polymerization. Most of the reported metal alkoxides/aryloxides described by the formulation $[(OR)_nMX_{4-n}]$

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[where R = alkoxo/aryloxo, X = labile ligand, M = Ti (IV)/Zr (IV)] are relatively ineffective in presence of MAO as co-catalyst for ethylene polymerization [11]. In an earlier work we demonstrated that fully substituted sterically bulky aryloxo complexes of Ti (IV) & Zr(IV) of the type $M(OR)_4$ in presence of different alkylaluminum co-catalysts (excluding MAO) were active for oligomerization of ethylene to linear α–olefins under optimum conditions [12]. In order to gain further insight into these type of catalysts in production of synthetic PE wax, in the present work we have focused on the complexes of Ti(IV) with sterically hindered yet versatile ligand 1,1′-binaphthalene 2, 2′-diol (Binol) and its derivative. Though the C_2 symmetric Binol has been extensively studied in asymmetric catalysis and other organic reactions its application in polyolefin synthesis to the best of our knowledge, has not been explored [13]. The axially chiral Binol ligand exhibits a diverse and often unpredictable range of bonding modes, particularly with Gr. IV metals such as Ti (IV) and Zr (IV) [14,15]. The propensity of inter and intramolecular ligand and Ti-fragment exchange in solution can lead to the formation of both monomeric as well as polynuclear oligomers, the existence of which is significantly influenced by reaction temperature and stoichiometry of starting reagents during synthesis [16]. We describe here our results on the preparation of $(Binol)_2Ti/(Binol)TiX_2$ complexes and their evaluation in catalytic ethylene polymerization in combination with ethylaluminum sesquichloride ($Et_3Al_2Cl_3$, EASC) as co-catalyst.

2. Experimental

2.1. Materials

All work involving air and/or moisture-sensitive compounds was carried out by using standard high vacuum Schlenk or dry box (VAC) techniques. Toluene was refluxed over sodium wire for 4 h and distilled before use. Polymer grade ethylene was used directly from commercial plant, the pressure of which was adjusted with a two stage regulator. Co-catalysts were purchased from Ethyl Corporation or Witco GmbH and used without further purification. Binol and its R/S enantiomers were prepared by a reported method [17].

2.2. Measurements

Microanalysis was carried out on a Perkin-Elmer Model 2400 instrument. Titanium content in catalysts was determined gravimetrically as TiO_2. A Perkin-Elmer FT-IR spectrometer model Spectrum BX was used to obtain the IR spectra of samples pressed into KBr pellets over 4000–400 cm^{-1} range. The ^1H NMR spectrum of catalysts was recorded in $CDCl_3$ solvent on a Varian NMR 300 MHz spectrometer using TMS as an internal reference. FAB mass spectral analysis of catalysts was carried out on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon as the FAB gas. The accelerated voltage was 10 kV and the spectra recorded at room temperature. *m*-Nitrobenzyl alcohol was used as the matrix. Molecular weights of polymers were determined using size exclusion chromatography (SEC). Samples were prepared for SEC analysis by drying the polymer in vacuum and dissolving 50 mg of the polymer in 10 mL of 1,2,4-trichlorobenzene (TCB, HPLC grade). The SEC instrument consisted of a Waters 717 plus auto sampler, a Waters 600E system controller connected to 410 RI detector maintained at 140 °C. TCB sparged with IR-grade helium was used as eluent at a flow rate of 1 mL/min. Four Phenogel columns (300–7.80 mm) with respective pore sizes of 100, 10^3, 10^4 and 10^5 Å were used in series. The system was calibrated using six narrow polystyrene molecular weight standards in the range 4000–100,000 supplied by Pressure Chemical Co., USA. All GPC analyses were carried out at 140 °C. Differential scanning calorimetry was performed under a continuous nitrogen purge on a Mettler-Toledo DSC 822 instrument from 30 to 200 °C at a scan rate of 10 °C/min. Indium was used to perform the calibration. TGA/DTA of catalysts were recorded in air (heating rate 10 °C/min) from ambient to 600 °C on a TA Instrument (Universal V2). Density of polymers was determined in *n*-butyl acetate medium at 23 °C as per ASTM method D 792-00. X-ray experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled Cu Kα radiation (λ = 1.5406 Å, generator voltage = 45 kV, current = 40 μA) in the reflection mode, detected by a scintillation counter. Samples were pressed films approximately 400 μm thick and were scanned into 2θ ranges from 15°–45° at a rate 1°/min. Measurement were recorded at steps of 0.02°. Scanning electron micrographs of polymer were taken on a CAMICA SU30 instrument with SE electrode at 20 kV.

2.3. Catalyst preparation

Catalysts **1**–**4** were synthesized by a modified literature procedure [15d,g]. To a solution of 1 mmol (284 mg) of $Ti(OPr^i)_4$ in toluene (25 mL) was added slowly 1 or 2 mmol (286 mg or 572 mg) of the corresponding bi-phenol ligand in warm toluene (30 mL) under nitrogen atmosphere and heated at 60 °C for 3 h. The contents were then stirred for 24 h at room temperature. The solvent was carefully removed, precipitated solid washed with small portions of warm toluene and finally the orange coloured complexes were isolated. Anal calc. for 1 ($C_{40}H_{24}O_4Ti$); C, 77.9; H, 3.9; Ti, 7.8; Found: C,77.3; H 3.4; Ti, 7.6. Similarly for **1a** ($C_{26}H_{26}O_4Ti$); C, 69.3; H, 5.8; Ti, 10.6; Found: C, 69.8; H, 6.0; Ti, 10.3.

2.4. Ethylene polymerization

Ethylene polymerization was conducted in a 600 mL stirred autoclave (Parr, USA) connected to a model 4850 microprocessor controller. Prior to polymerization, the reactor was heated to 150 °C under nitrogen for 2 h and cooled to ambient temperature. In a typical experiment catalyst

1 (9.6 mg, 0.0155 mmol) dissolved in 50 mL toluene and EASC (0.85 mL, 3.1 mmol) in toluene (200 mL) were carefully charged into the reactor under a nitrogen blanket. The reactor temperature was kept at 100 °C and then pressurized with ethylene to 200 psi. The reaction was continued for 1 h, cooled, degassed and the slurry slowly poured into acidic methanol (5%, v/v) to precipitate the polymer. The white polyethylene powder was filtered, washed several times with methanol followed by acetone and finally dried under reduced pressure at 60 °C.

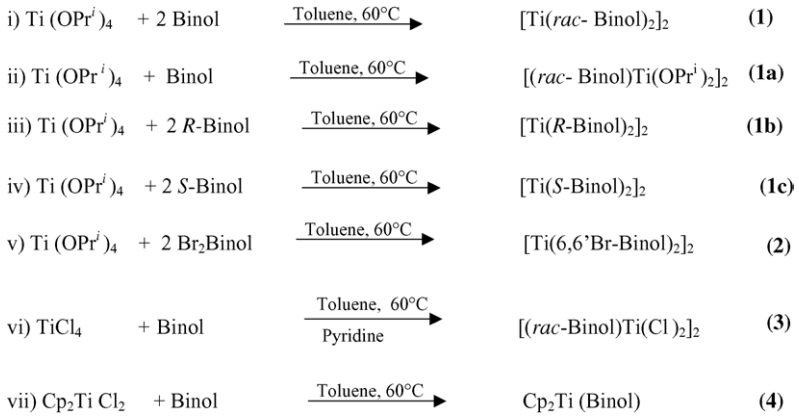
3. Results and discussion

3.1. Synthesis of Ti(IV) complexes with Binol and its derivatives

The protocol for the preparation of Ti-Binolate complexes could be realized via one of the following three synthetic routes (a) stoichiometric reaction between titanium tetraisopropoxide and racemic or (R)/(S)-Binol ligand (alcohol exchange) and separation of liberated *iso*-propanol by (azeotropic/vacuum distillation) [18], b) treatment of a lithium salt of Binol with titanium tetrachloride followed by removal of LiCl [15] and (c) low temperature reaction between the diol ligand and titanium tetrachloride in presence of a base (usually tertiary amine) for eliminating the HCl formed [11]. Method (a) was chosen in this work for isolating the Ti-Binol catalysts **1**–**4** (Scheme 1) as it proved to be convenient for working with toluene as solvent for polymerization of ethylene. Moreover, the complex could be isolated in fewer steps than with methods (b) or (c).

3.2. Catalyst characterization

The stoichiometric reaction between $Ti(OPr^i)_4$ and Binol ligand in toluene solution afforded dark orange coloured complexes. Both the 1:1 and 1:2 complexes $Ti(Binol)(OPr^i)_2$ (**1a**) and $Ti(Binol)_2$ (**1**) are soluble in aromatic solvents but only sparingly so in aliphatic hydrocarbons. Depending on the molar ratio of the starting $Ti(OPr^i)_4$ and the Binol derivative a variety of complexes have been isolated previously by Heppert and Walsh, a limited number of which have been characterized by X-ray crystal structure analysis [15,16]. Catalysts **1a** has been shown to exist as a dimer in the solid state based on X-ray analysis [19]. Catalysts **3** and **4** were isolated as orange coloured microcrystalline powders in moderate yields by reacting $TiCl_4$ or Cp_2TiCl_2 and an equimolar solution of H_2Binol ligand. Stable complexes of the type $Cp_2Ti(O\text{^}O)$ (where O^O = catechol) have previously been isolated employing method (c) [20]. The Ti-binolate catalysts have been characterized by microanalysis, ^{1}H NMR, FAB mass spectra and thermal analysis. The ^{1}H NMR spectra are generally simple and was primarily used as a diagnostic tool for ascertaining the purity of complexes (Fig. 1). A set of multiplets in the region 7.5–8.5 ppm for the aromatic protons was a common feature and in case of **1a** additional signals due to methyl protons of *iso* propyl group (1–1.2 ppm) were observed. A small trace of starting material H_2Binol was detected in complex **1**/**1a** despite repeated washings while purifying the catalyst. In the FAB mass spectra of **1** (Fig. 2) the parent ion appears at 616 (cal. 617) with low intensity peak for the diol fragment at 286. However, in the case of **1a** the parent ion was not detected but the highest observed molecular weight ion at 391 was assigned to $Ti(Binol)(OPr^i)^+$ species which corresponds to parent ion minus coordinated alkoxide. Fragment ions originating from dimeric or trimeric species were difficult to establish due to complexity of the spectrum beyond *m/z* values of 600. Similar band pattern was noted in the EI-MS of other dimeric titanium alkoxide complexes [21–23]. Recognizing the fact that intra- and intermolecular rearrangement of alkoxide groups in binaphtholate Ti(IV) complexes lead to different structural behavior in solution as well as in solid state we proceeded to examine these catalysts by thermal analysis. We hypothised that the solid state thermal degradation profile might provide some insight that could help ascertain the composition fixed on the basis of analytical and ^{1}H NMR data. Catalysts **1**–**4** were heated at a



Scheme 1. Synthesis of Ti-binolate complexes.

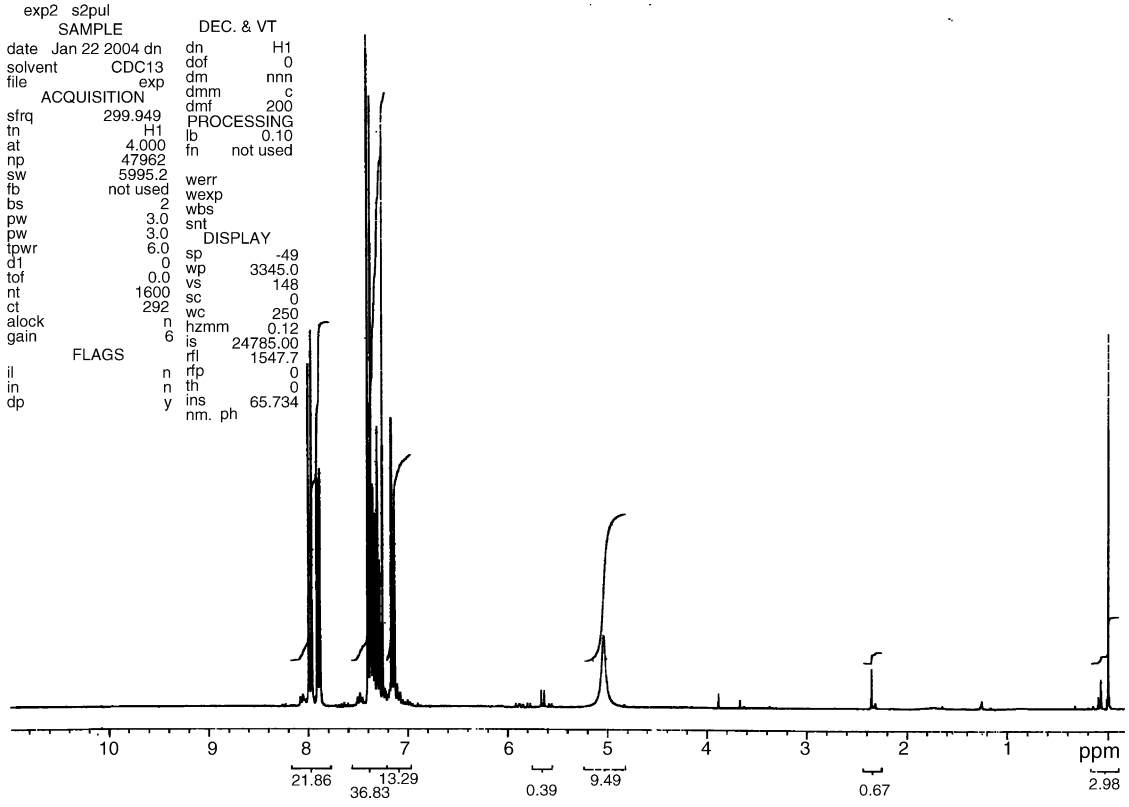


Fig. 1. ^{1}H NMR of catalyst **1**.

predetermined rate from ambient to 600 °C. In a typical DTA profile (Fig. 3) only two major peaks could be seen between 300 and 600 °C. Using the percentage weight loss on the thermogram an attempt was made to assign the possible species corresponding to the observed loss. These results are summarized in Table 1. In most cases it was possible to correlate the observed weight loss during thermal decomposition with the empirical formulation [22].

3.3. Polymerization of ethylene

The results of ethylene polymerization using catalyst precursors **1**–**4** are shown in Table 2. The efficiency of catalysts was compared with the known metallocene catalysts Cp_2TiCl_2 and Cp_2ZrCl_2 in presence of EASC as co-catalyst. The polymerization was carried out under different reaction conditions such as temperature, Al/Ti ratio, pressure,

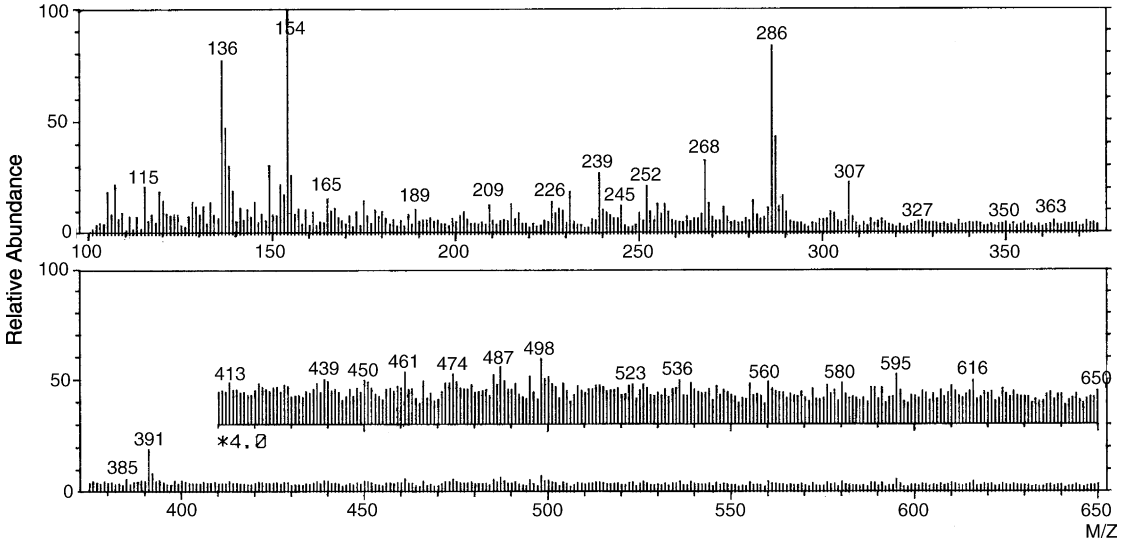


Fig. 2. Mass spectra of catalyst **1**.

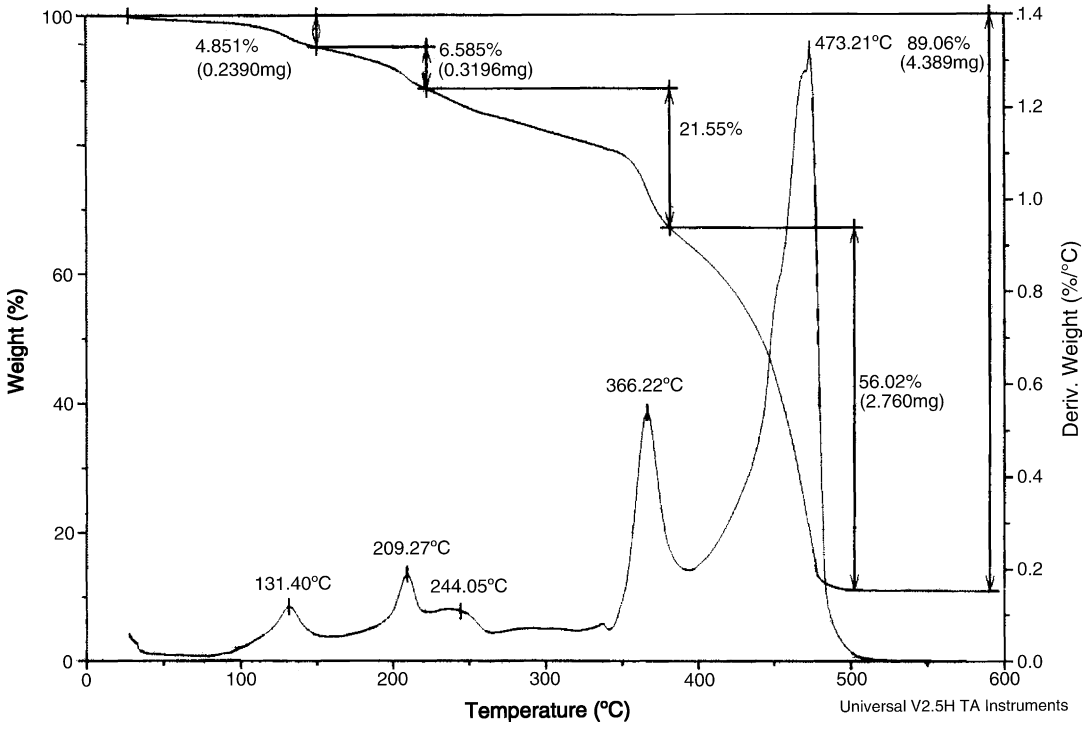


Fig. 3. Typical TG/DTA of catalyst **1**.

Table 1
Thermal degradation study of selected catalysts

Catalyst	M. wt.	Degradation temp (°C)	% wt. loss observed	% wt. loss estimated	Fragment assigned
1	616.6	366	21.6	23	Naphthyl
		473	56	46	Binolate
1a	450.5	423	73	76	OPr^i + binol
		437	84	89	TiO_2 (residual)
2	932	375	28	32	2 Br + binol
		433	64	62.8	Br binol
		453	92	94.8	TiO_2 (residual)
3	403	277	47.5	52	2Cl + naphthyl
		346	36.5	35.2	Naphthyl
		458	84.2	87.9	TiO_2 (residual)
4	462	315	26.7	28	2Cp
		454	62.0	61.5	Binol
		545	88.7	89.5	TiO_2 (residual)

Table 2
Ethylene polymerization with Ti-diolate–EASC catalyst system[a]

Entry	Catalyst	Yield (g)	Activity (kg PE/g Ti)	M_w	PD	T_m (°C)	d (g/cc)
1	**1**	8.53	11.5	1800	1.8	118	0.963
2	**1a**	4.84	6.8	2700	2.6	124	0.955
3	**1b**	7.5	10.5	3300	2.6	128	0.952
4	**1c**	7.2	10.1	3200	2.5	127	0.955
5	**2**	7.93	11.1	3400	2.4	126	0.954
6	**3**	3.22	4.5	2800	2.2	126	0.960
7	**4**	0.67	0.9	–	–	–	0.940
8	Cp_2TiCl_2	0.16	0.22	–	–	–	–
9	Cp_2ZrCl_2	0.68	0.93	–	–	–	–

[a] All reactions were carried out in a 600 mL SS reactor at 100 °C and 200 psi ethylene pressure for 1 h.

Table 3
Effect of co-catalysts on ethylene polymerization at 100 °C

Entry	Co-catalyst[a]	Yield (g)	Activity (kg PE/g Ti)	T_m (°C)
1	DEAC	1.51	2.1	125
2	EADC	1.97	2.7	–
3	EASC	8.35	11.5	118
4	MAO	1.55	1.1	131
5	TEAL	0.03	0.05	–
6	TIBAO	0.41	0.6	–

[a] DEAC = Et_2AlCl, EADC = $EtAlCl_2$, TIBAO = tri isobutyl alumoxane catalyst **1**, $^pC_2H_4$ = 200 psi.

solvent and co-catalysts. Our initial examination of catalysts indicate that amongst the different diols, the titanium complexes of Binol derivatives with 1:2 stoichiometry generally display higher activity in polymerization (**1**, **1b**, **1c**, **2**) compared to 1:1 complex (**1a**, **3**). The metallocenes on the other hand are practically inactive under these reaction conditions (Table 2, entry 8, 9). The activity is also predominantly dependent on the nature of the co-catalyst. Ethyl aluminum sesquichloride uniquely favours the polymerization. Other chlorinated alkyl aluminums Et_2AlCl (DEAC) and $EtAlCl_2$ (EADC) are also active but with lowering of productivities. This rather exclusive combination of Ti-diolate precursor and EASC co-catalyst in polymerization suggests formation of active intermediates responsible for polymerization as will be discussed in the following section. Interestingly amongst the conventional co-catalysts for polyolefin production such as MAO & Et_3Al only the former shows moderate activity while triethylaluminum is practically inactive (Table 3). A noteworthy feature of polyethylene obtained with these Ti-diolate catalysts is the invariably low molecular weight (M_w) of the polymer as revealed by GPC analysis. In all cases the PE's display narrow molecular weight distribution (M_w/M_n = 1.8–2.6). The bromo-Binol derivative **2** has nearly similar activity than the unsubstituted complex **1** but displays higher M_w and melt behaviour. Though the effect of substituted Binol and its catalytic activity is not very clearly understood at present, it is, however, pertinent to point out that the monosubstituted aryloxides of titanium such as $Ti(OR)_4$ essentially lead to low molecular weight linear alpha olefins in the C_4–C_{20} carbon range in sharp contrast to the exclusive formation of solid polyethylene with sterically bulky bidentate $Ti(O\hat{}O)_2$ type complexes employed in the present study [11d]. This can be qualitatively interpreted as $r_p \cong r_t$ in the case of $Ti(OR)_4$-EASC catalyst system resulting in oligomer formation whereas with $Ti(O\hat{}O)_2$ -EASC system $r_p > r_t$ giving polyethylene under identical conditions. The absence of ethylene oligomers in the solution was also confirmed by GC at the end of reaction. Detailed studies on the effect of temperature and pressure were then carried out employing complex **1** & EASC as the co-catalyst. From the results summarized in Table 4 it is evident that increasing the reaction temperature from ambient to 100 °C has marked effect on the activity (Table 4, entry 1 and 3). The effect of ethylene pressure has been compiled in Table 5. Optimum pressure for

Table 4
Effect of temperature on polymerization[a]

Entry	Temp (°C)	Yield (g)	Activity (kg PE/g Ti)	M_w	PD	T_m (°C)
1	27	2.37	2.84	2200	2.4	129
2	50	2.07	3.35	2100	2.6	120
3	100	8.35	11.47	1800	2.0	118

[a] Catalyst **1**-EASC, $^pC_2H_4$ = 200 psi.

Table 5
Effect of pressure on ethylene polymerization[a]

Entry	$^pC_2H_4$ (psi)	Yield (g)	Activity (kg PE/g Ti)	M_w	PD	T_m (°C)
1	100	4.33	5.9	2300	2.4	123
2	200	8.35	11.5	1800	1.8	118
3	300	1.71	2.3	2650	2.5	132
4	500	1.63	2.2	–	–	–

[a] Catalyst **1**-EASC, Temp = 100 °C.

good activity was around 200 psi at 100 °C and Al/Ti ratio of 200 (Table 5, entry 2). Surprisingly applying higher pressure under similar condition does not lead to higher productivity (Table 5, entry 4). Interdependence of Al/Ti and temperature has been separately investigated (Table 6). Generally a combination of higher Al/Ti ratio and higher temperature lead to improvement in productivity of the catalyst.

Preliminary study of the reactivity of different olefins towards polymerization with **1**/EASC were attempted. Interestingly propylene and butene-1 polymerization lead to the formation of low molecular weight liquid oligomers in the slurry. We believe that for these higher olefins increase in bulk of the α-olefin may hinder the monomer insertion in to the Ti-diolate catalytic species during chain propagation step leading to high molecular weight polymer. A brief examination of effect of different solvents indicated that chlorinated aromatic solvent such as chlorobenzene gave a two fold increase in productivity of polyethylene than that observed for toluene. However, aliphatic hydrocarbon solvents such as hexane or heptane resulted in poor activity which may be due to low solubility of catalysts in these solvents.

To investigate the properties of polyethylene waxes reported in Table 2 they were characterized by GPC (Fig. 4). In the GPC a major peak (M_w) centered around 2000 is observed. However, closer examination revealed that in a few cases (b, c and d) a small shoulder appears in the low molecular weight region. This means there might be more than one type of catalytic species leading to bimodal

Table 6
Influence of Al/Ti ratio and temperature on polymerization[a]

Entry	Al/Ti ratio	Temp (°C)	Yield (g)	Activity (kg PE/g Ti)
1	60	100	6.98	6.59
2	60	50	1.71	2.34
3	200	100	9.55	11.5
4	200	50	2.88	3.9
5	200	27	2.37	2.84

[a] Catalyst **1**-EASC, $^pC_2H_4$ = 200 psi.

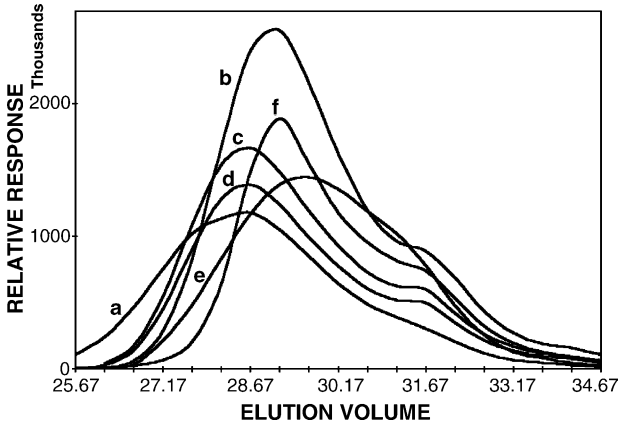


Fig. 4. GPC profiles of polymer listed in Table 2: (a) entry 5, (b) entry 2, (c) entry 4, (d) entry 3, (e) entry 1, (f) reference sample.

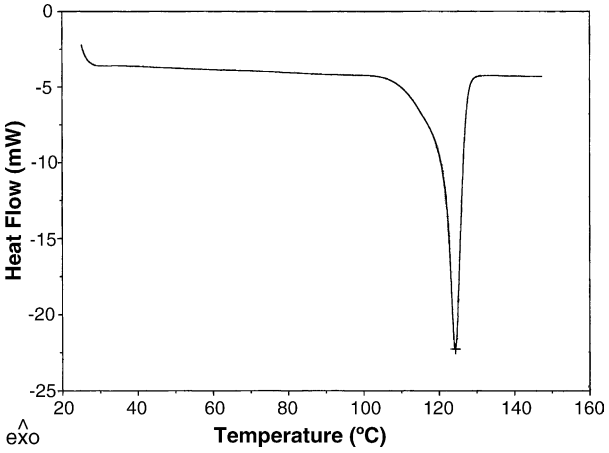


Fig. 6. Representative DSC of PE wax sample (Table 2, entry 2).

type of distribution. A commercial PE wax sample was also included as a reference for comparison. GPC of this material also displays similar distribution in the low molecular weight region. An attempt was made to analyze these plots by deconvoluting the GPC. For instance the GPC of sample 'd' was resolved by a PeakFit software and the result is depicted in Fig. 5. Based on the integration of area under individual peaks it was found that the low molecular weight fraction corresponds to ~12 wt.% (M_w = 670–700). Surprisingly this fraction does not show any secondary peak in the DSC (T_m). It is possible that this small percentage of low molecular weight fraction does not significantly influence the crystallinity of the wax hence the T_m shows a single sharp melting peak in the region from 80–130 °C. As mentioned earlier one of the striking feature of these PE's is the exceptionally low molecular weights (M_w = 1800–3400) and narrow polydispersities (PD = 1.8–2.6). In no case was high molecular weight PE ($\sim M_w \geq 10^5$) obtained though these catalysts resemble typical Ziegler systems. As described in the introduction polyethylene waxes with interesting applications have similar molecular weights and molecular weight distribution [24]. The DSC (Fig. 6) also reveals lower T_m values than that observed for conventional HDPE or LDPE. As a benchmark for comparison of polymer properties with that obtained in this work a known sample of micronized PE-wax was used [24]. The intensity of the equatorial peaks in the X-ray diffractogram (Fig. 7) for the 110 (2θ = 21.6°) and 200 (2θ = 24°) reflection planes for the experimental sample closely match the intensity of the reference sample and the pattern is indicative of orthorhombic crystallinity in these samples.

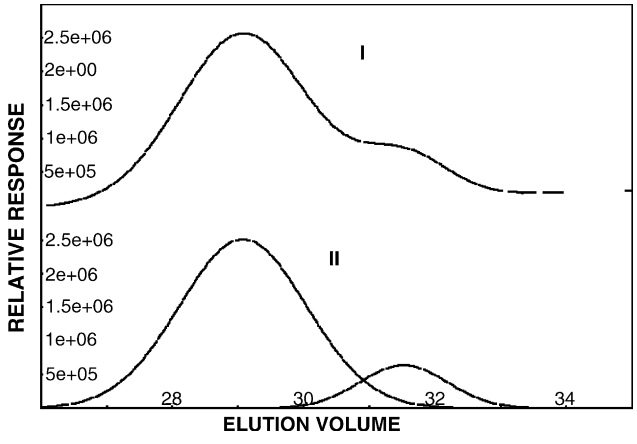


Fig. 5. Experimental (**I**) and deconvoluted (**II**) GPC trace for a bimodal PE wax (ref. 'd' in Fig. 4; r^2 = 0.9893, Peak Fit Software).

The crystalline nature of these polymers is also supported by the extent of crystallinity determined from heat of fusion (integration of the DSC exotherm) which was generally in the

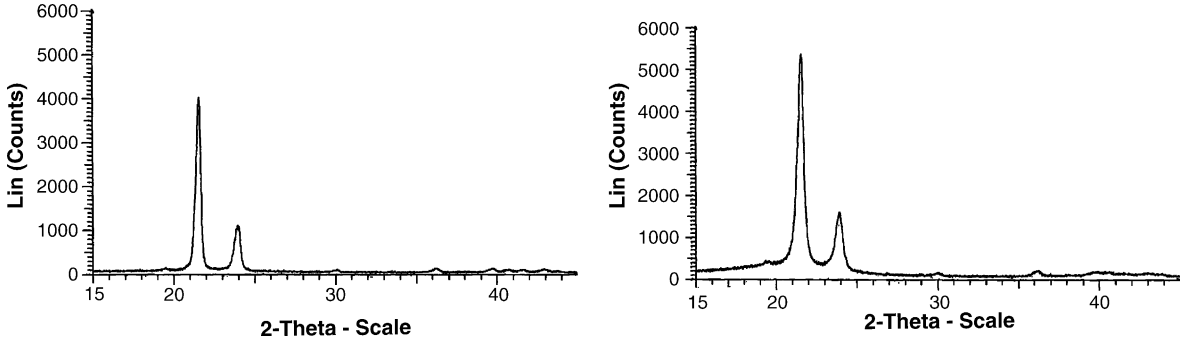


Fig. 7. XRD of PE wax (Table 2, entry 1) and reference sample.

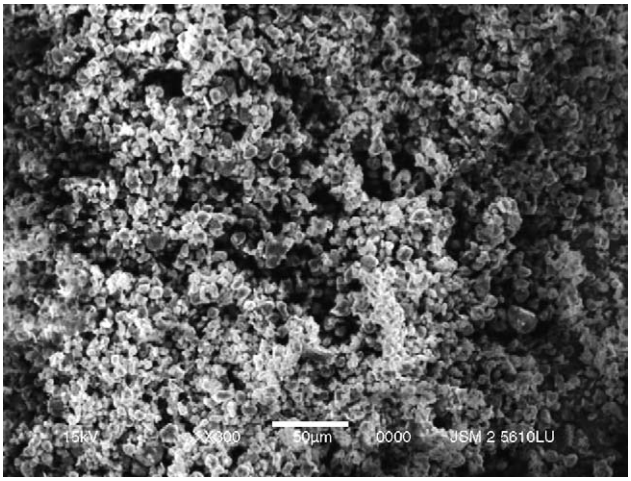
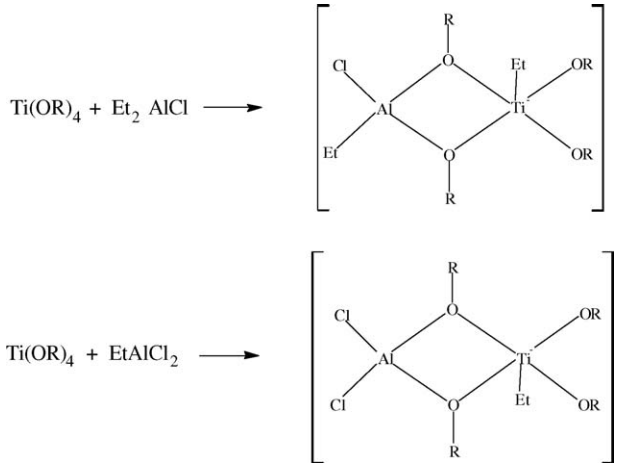


Fig. 8. SEM of PE wax (Table 2, entry 1).

range of 70–83%. The polymer particles are fine and have uniform morphology as seen by Scanning Electron Micrograph. A typical SEM is reproduced in Fig. 8. The unique wax like polymer obtained by these titanium-diolate–EASC catalyst system can be fine tuned to tailor the M_w and polydispersities as per requirement of its end use application.

3.4. Catalytic pathway

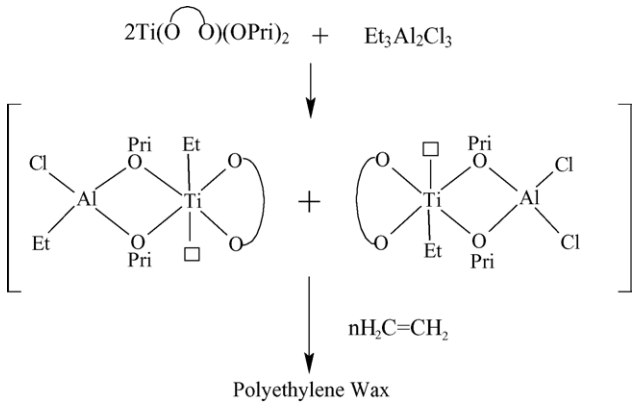
Treatment of mononuclear $Ti(OR)_4$ type alkoxides with alkylaluminum halides has been reported to yield active intermediates responsible for the polymerization of ethylene to low molecular weight products [25,26].



We believe that similar type of active species may be involved in the present Ti-Binol system. Moreover, as EASC is derived from an equimolar mixture of EADC and DEAC [27], we have

$$2Et_3Al_2Cl_3 \rightleftharpoons (EtAlCl_2)_2 + (Et_2AlCl)_2$$

Since EASC can dissociate as Et_2AlCl and $EtAlCl_2$ in solution it is reasonable to expect the formation of two type of catalytic species on interaction with Ti-binolate catalyst.



Scheme 2. Proposed reaction pathway.

The reduction of Ti(IV) in presence of EASC will generate catalytically active components. As shown in Scheme 2 the active catalysts in polymerization need to retain monomeric four or five coordinate geometry to allow for olefin insertion and subsequent propagation [28]. In the present Ti-binolate catalytic system higher temperatures tend to favour formation of active intermediates responsible for polymerization. Based on this hypothesis it is possible to predict the pathway shown in Scheme 2 for the formation of polyethylene wax.

Though the structure of active intermediate is as yet unknown the mechanism leading to polyethylene is consistent with those reported previously for solution phase olefin polymerization using titanium alkoxides and aluminum alkyls [11,29,30]. Efforts are underway to investigate the detailed kinetics of this reaction.

4. Conclusions

The titanium (IV) binolate-$Et_3Al_2Cl_3$ was found to be a simple and versatile catalyst system for the synthesis of specialty low molecular weight polyethylene with good productivity. The complexes can be synthesized conveniently from readily available starting materials. The unique polymer characteristics such as lower molecular weights, high crystallinity and narrow dispersities exhibited by polyethylenes obtained with these catalysts closely resemble the properties of commercially important synthetic waxes. Higher temperatures and higher Al/Ti ratio significantly influence the rate of reaction and catalyst activity.

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Appendix A. Supplementary information

^{1}H NMR, FAB mass, TGA/DTA of catalyst **1a** and XRD, SEM of PE wax (Table 2, entry 2) are provided as supporting figures.

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2005.06.067.

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