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1. Synthesis of low molecular weight polyethylene waxes by titanium BINOLate–ethylaluminium sesquicatalyst system.

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2. Controlled synthesis of low molecular weight polyethylene waxes by Ti-Biphenolate $-Et_3Al_2Cl_3$ based catalyst systems.

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3. Catalytic ring-opening polymerization of l-Lactide by Titanium biphenoxy-alkoxide initiators.

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4. Polyethylene waxes : catalytic synthesis by Ti-Biphenolates.

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5. Synthesis of low molecular weight polyethylene by S – bridged Ti complexes.

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*Reaction Kinet. and Catal. Lett.,* In Press (2007).

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7. Ultra low molecular weight polyethylene : Synthesis using Ti-Biaryloxy catalysts

**P. S. Umare**, K. V. Rao , G. L. Tembe, D. A. Dhoble , B. Trivedi.

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8. Catalytic oxidative coupling of 2-Naphthol using metal β-diketonates.

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

P.S. Umare [a], R. Antony [b], K. Gopalakrishnan [b], G.L. Tembe [b,*], B. Trivedi [a]

[a] *Department of Chemistry, The M.S. University of Baroda, Vadodara 390 002, India*
[b] *Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India*

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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.


*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 $[(OR)_nMX_{4-n}]$

* Corresponding author. Tel.: +91 265 3062255; fax: +91 265 3062104.
*E-mail address:* gopal.tembe@ipcl.co.in (G.L. Tembe).

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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 hol was used as the matrix. Molecular weights of mers were determined using size exclusion chromatog (SEC). Samples were prepared for SEC analysis by dryi polymer in vacuum and dissolving 50 mg of the polyı 10 mL of 1,2,4-trichlorobenzene (TCB, HPLC grade SEC instrument consisted of a Waters 717 plus autc pler, a Waters 600E system controller connected to 4 detector maintained at 140 °C. TCB sparged with IR helium was used as eluent at a flow rate of 1 mL/min Phenogel columns (300–7.80 mm) with respective por of 100, $10^3$, $10^4$ and $10^5$ Å were used in series. Th tem was calibrated using six narrow polystyrene mol weight standards in the range 4000–100,000 suppli Pressure Chemical Co., USA. All GPC analyses wei ried out at 140 °C. Differential scanning calorimetr performed under a continuous nitrogen purge on a M Toledo DSC 822 instrument from 30 to 200 °C at rate of 10 °C/min. Indium was used to perform the c tion. TGA/DTA of catalysts were recorded in air (heati 10 °C/min) from ambient to 600 °C on a TA Instrumen versal V2). Density of polymers was determined in r acetate medium at 23 °C as per ASTM method D 792- ray experiments were carried out on a Brüker AXS mo advanced diffractometer. Scattering patterns were ob with Ni-filled Cu Kα radiation (λ = 1.5406 Å, generatc age = 45 kV, current = 40 μA) in the reflection mode, de by a scintillation counter. Samples were pressed films a imately 400 μm thick and were scanned into $2\theta$ range 15°–45° at a rate 1°/min. Measurement were recorded ε of 0.02°. Scanning electron micrographs of polyme taken on a CAMICA SU30 instrument with SE electı 20 kV.

### 2.3. Catalyst preparation

Catalysts **1–4** were synthesized by a modified lit procedure [15d,g]. To a solution of 1 mmol (284 r $Ti(OPr^i)_4$ in toluene (25 mL) was added slowly 1 or 2 (286 mg or 572 mg) of the corresponding bi-phenol lig warm toluene (30 mL) under nitrogen atmosphere and at 60 °C for 3 h. The contents were then stirred for room temperature. The solvent was carefully remove cipitated solid washed with small portions of warm t and finally the orange coloured complexes were is Anal calc. for 1 ($C_{40}H_{24}O_4Ti$); C, 77.9; H, 3.9; Ti, 7.8; C,77.3; H 3.4; Ti, 7.6. Similarly for **1a** ($C_{26}H_{26}O_4Ti$); C 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 ( stirred autoclave (Parr, USA) connected to a mode microprocessor controller. Prior to polymerization, th tor was heated to 150 °C under nitrogen for 2 h and to ambient temperature. In a typical experiment (

l (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.

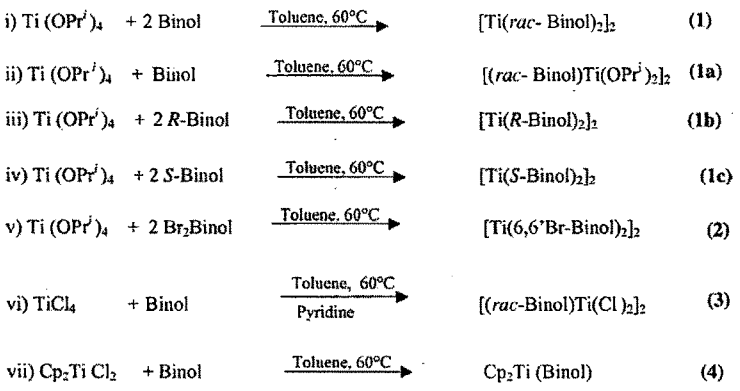
## 3. Results and discussion

### 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 $H_2$Binol ligand. Stable complexes of the type $Cp_2Ti(O\hat{}O)$ (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 $H_2$Binol 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.

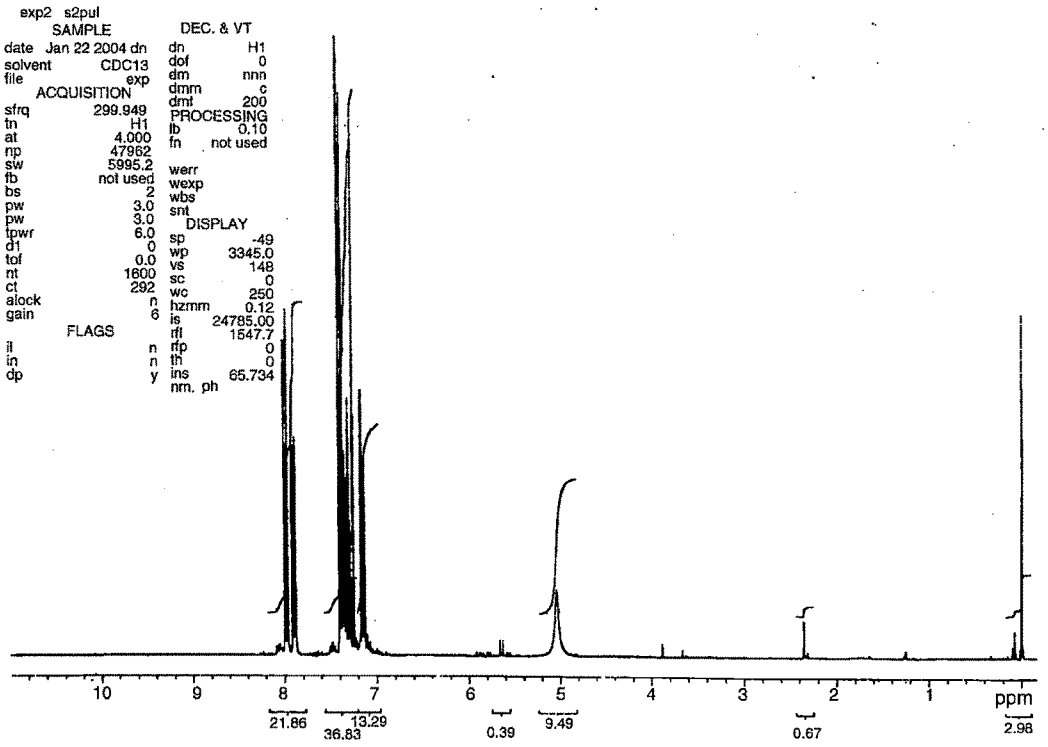



Fig. 1. $^1$H NMR of catalyst 1.

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 cataly cursors **1–4** are shown in Table 2. The efficiency o lysts was compared with the known metallocene ca $Cp_2TiCl_2$ and $Cp_2ZrCl_2$ in presence of EASC as co-ca The polymerization was carried out under different tion conditions such as temperature, Al/Ti ratio, pr

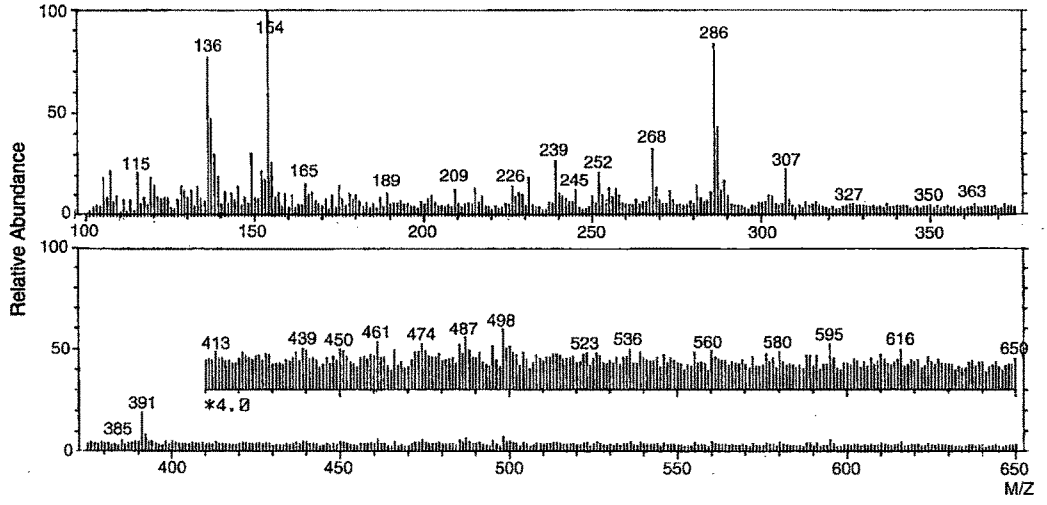



Fig. 2. Mass spectra of catalyst 1.

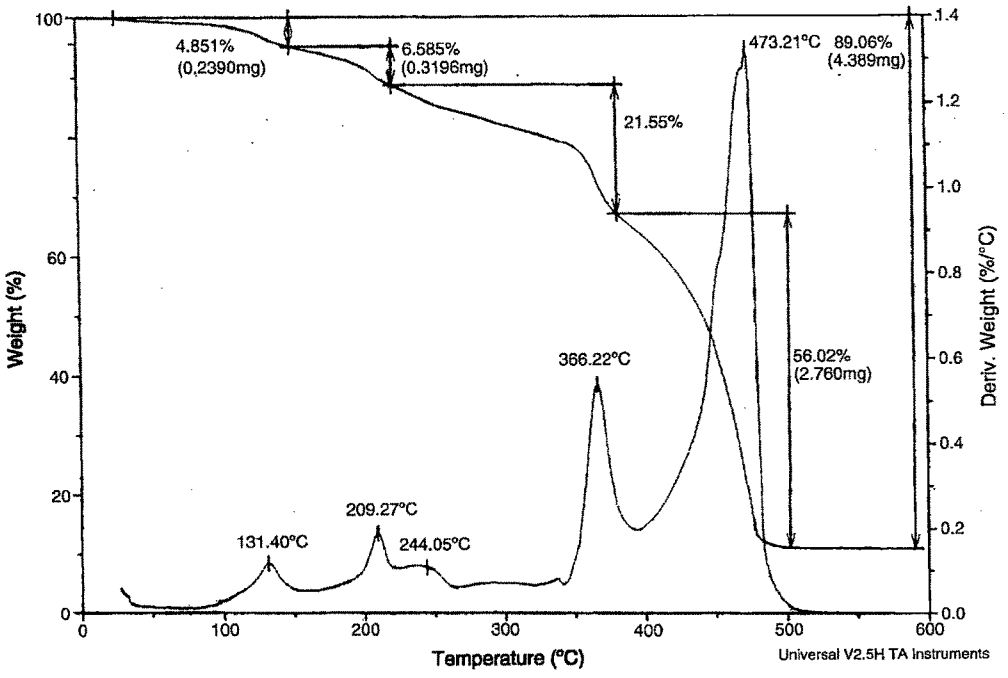



Fig. 3. Typical TG/DTA of catalyst **1**.

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**, $^{P}C_2H_4$ = 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 $Ti(O^{\wedge}O)_2$ 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 $Ti(O^{\wedge}O)_2$-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 |
|---|---|---|---|---|---|---|
| 1 | 27 | 2.37 | 2.84 | 2200 | 2.4 | 1 |
| 2 | 50 | 2.07 | 3.35 | 2100 | 2.6 | 1 |
| 3 | 100 | 8.35 | 11.47 | 1800 | 2.0 | 1 |

[a] Catalyst **1**-EASC, $^{P}C_2H_4$ = 200 psi.

Table 5
Effect of pressure on ethylene polymerization[a]

| Entry | $^{P}C_2H_4$ (psi) | Yield (g) | Activity (kg PE/g Ti) | $M_w$ | PD | T |
|---|---|---|---|---|---|---|
| 1 | 100 | 4.33 | 5.9 | 2300 | 2.4 | |
| 2 | 200 | 8.35 | 11.5 | 1800 | 1.8 | |
| 3 | 300 | 1.71 | 2.3 | 2650 | 2.5 | |
| 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 r
200 (Table 5, entry 2). Surprisingly applying higher pr
under similar condition does not lead to higher produ
(Table 5, entry 4). Interdependence of Al/Ti and tempe
has been separately investigated (Table 6). Generally a
bination of higher Al/Ti ratio and higher temperature l
improvement in productivity of the catalyst.

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

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

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

| Entry | Al/Ti ratio | Temp (°C) | Yield (g) | Activity (kg |
|---|---|---|---|---|
| 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, $^{P}C_2H_4$ = 200 psi.

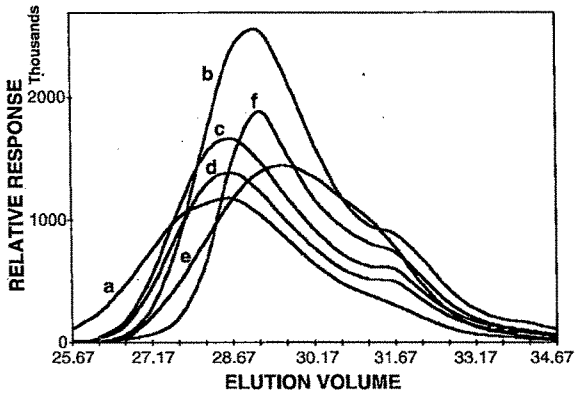



Fig. 4. GPC profiles of polymer listed in Table 2: (a) entry 5, (b) entry 2, (c) entry 4, (d) entry 3, (e) entry 1, (f) reference sample.

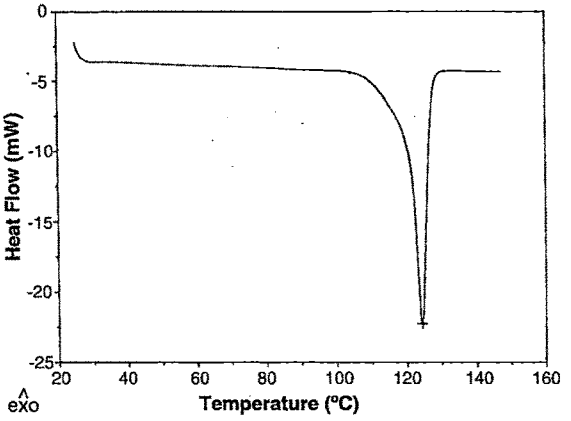



Fig. 6. Representative DSC of PE wax sample (Table 2, entry 2).

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 ($2\theta$ = 21.6°) and 200 ($2\theta$ = 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.

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

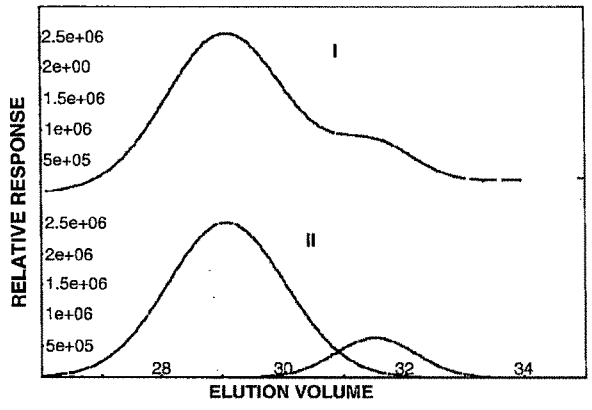



Fig. 5. Experimental (I) and deconvoluted (II) GPC trace for a bimodal PE wax (ref. 'd' in Fig. 4; $r^2$ = 0.9893, Peak Fit Software).

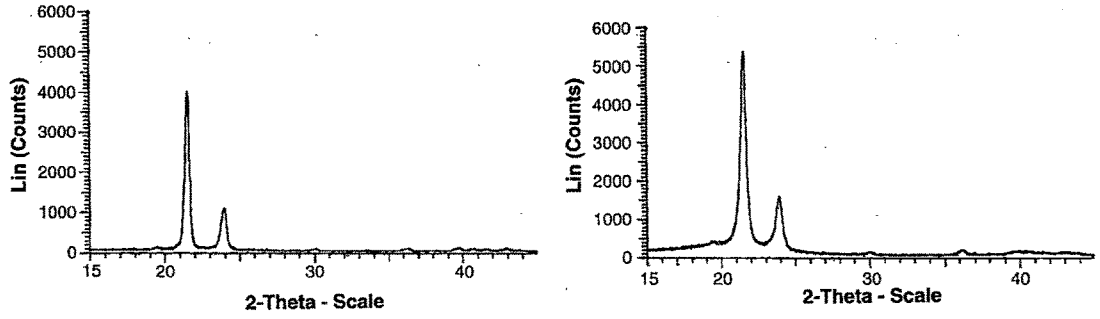



Fig. 7. XRD of PE wax (Table 2, entry 1) and reference sample.

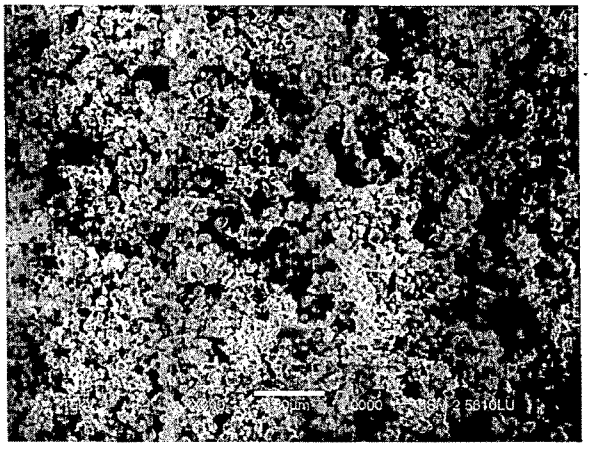
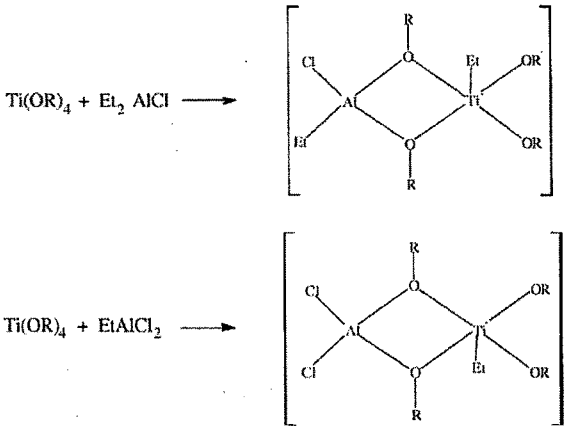


Fig. 8. SEM of PE wax (Table 2, entry 1).

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

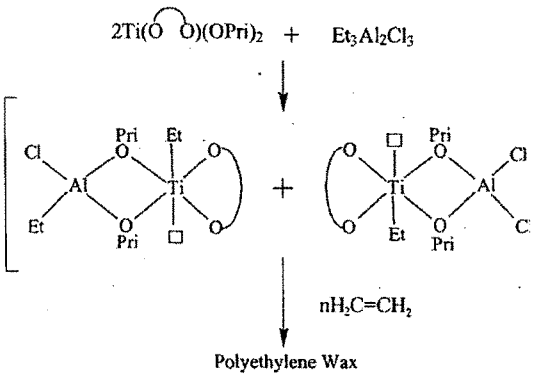
Treatment of mononuclear $Ti(OR)_4$ type alkoxides with alkylaluminum halides has been reported to yield active intermediates responsible for the polymerization of ethylene to low molecular weight products [25,26].




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 ge catalytically active components. As shown in Scheme active catalysts in polymerization need to retain monc four or five coordinate geometry to allow for olefin ins and subsequent propagation [28]. In the present Ti-bi catalytic system higher temperatures tend to favour f tion of active intermediates responsible for polymeriz Based on this hypothesis it is possible to predict the way shown in Scheme 2 for the formation of polyetl wax.

Though the structure of active intermediate is unknown the mechanism leading to polyethylene i sistent with those reported previously for solution olefin polymerization using titanium alkoxides and alur alkyls [11,29,30]. Efforts are underway to investiga detailed kinetics of this reaction.

## 4. Conclusions

The titanium (IV) binolate-$Et_3Al_2Cl_3$ was found a simple and versatile catalyst system for the s sis of specialty low molecular weight polyethylen good productivity. The complexes can be synthesize veniently from readily available starting material unique polymer characteristics such as lower mo weights, high crystallinity and narrow dispersities ited by polyethylenes obtained with these catalysts resemble the properties of commercially importan thetic waxes. Higher temperatures and higher Al/T significantly influence the rate of reaction and c activity.

## Acknowledgements

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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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# Controlled Synthesis of Low-Molecular-Weight Polyethylene Waxes by Titanium–Biphenolate–Ethylaluminum Sesquichloride Based Catalyst Systems

**Prashant S. Umare,[1] Karumanchi Rao,[2] Gopal L. Tembe,[2] Deepa A. Dhoble,[3] Bhavna Trivedi[1]**

[1]*Department of Chemistry, The M. S. University of Baroda, Vadodara 390 002, India*
[2]*Research Centre, Indian Petrochemicals Corporation, Limited, Vadodara 391 346, India*
[3]*Division of Polymer Science and Engineering, National Chemical Laboratory, Pune 411008, India*

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**ABSTRACT:** Soluble complexes of titanium(IV) bearing sterically hindered biphenols, such as biphenol, 1,1′-methylene di-2-naphthol, 2,2′-methylene bis(4-chlorophenol), 2,2′-methylene bis(6-*tert*-butyl-4-ethyl phenol), and 2,2′ ethylidene bis(4,6-di-*tert*-butyl phenol), were prepared and characterized. These catalyst precursors, formulated as [Ti(O^O)$X_2$], were active in the polymerization of ethylene at high temperatures in combination with ethylaluminum sesquichloride as a cocatalyst. The ultra-low-molecular-weight polyethylenes (PEs) were linear and crystalline and displayed narrow polydispersities. The catalytic polymerization leading to PE waxes in this reaction exhibited unique properties that have potential applications in surface coatings and adhesive formulations. © 2007 Wiley Periodicals, Inc. J Appl Polym Sci 104: 1531–1539, 2007

**Key words:** catalysts; polyethylene (PE); synthesis; Ziegler-Natta polymerization

## INTRODUCTION

The production of polyethylene (PE), a commodity polyolefin, has witnessed rapid growth in catalyst and manufacturing technologies over the last decade. Conventional Ziegler-based catalysts are used to make high-molecular-weight PEs with essentially broad molecular weight distributions, whereas single-site metallocenes yield linear PEs with fewer side chain branches and can be designed to yield polymers with predictable and desired molecular characteristics. Because of the industrial importance of new types of PEs as building blocks in the chemical industry, catalyst systems that are more active and selective are constantly being sought to match the demands of polymer properties and to minimize the costs of production. In the case of ethylene, apart from conventional grades, such as low-density PE and high-density PE, a potentially emerging segment of the global PE business involves the production of specialty ultra-low-molecular-weight PE waxes ($C_{40}$–$C_{100}$), which are gaining importance for many applications.[1–3] Commercial PE waxes, because of their unique physicochemical properties, serve as aids in a variety of plastics processing applications to enhance lubricity, control the set/softening point of hot-melt adhesives, impart slip and rub resistance in printing inks, improve the fusing properties in toner formulations, and so on.[4,5]

Synthetic PE waxes are generally characterized by lower melting temperatures ($T_m$'s), high crystallinities, molecular weights from 1000 to 3000 g/mol, and mean particle sizes around 10–30 μ for end use. Thus, a major strategy for the precise control of the molecular weights and polydispersity [PD = weight-average molecular weight ($M_w$)/number-average molecular weight ($M_n$)] of PE involves the design of suitable catalysts and olefin polymerization under controlled conditions. Industrially, PE waxes can be obtained by the cracking of petroleum naphtha or Fischer–Tropsch synthesis and by the polymerization of ethylene with typical polyolefin catalysts. Wax producers, such as Clariant (Licowax), Dow (Insite catalyst), and Mitsui (Excerex process), use proprietary metallocenes and methyl alumoxane (MAO) as a cocatalyst for the polymerization of ethylene to highly crystalline low-molecular-weight PE.[6–8] Compared to the relatively expensive metallocene technology, the design and development of nonmetallocene homogeneous catalysts that are easily accessible, less expensive, and stable to moisture for the production of specialty PE waxes constitutes a useful research objective.

Recent literature has indicated an increase in the application of new families of non-Cp-based catalyst precursors for ethylene polymerization. These have

*Correspondence to:* G. L. Tembe (gopal.tembe@ipcl.co.in).

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mainly led to high-molecular-weight PE or, in some instances, linear α-olefins with moderate to good selectivities.[9,10] The most notable catalysts in this category use tridentate (N—N—N) and bidentate (O—N) Schiff-base complexes of late transition metals.[11,12]

However, there have been no systematic efforts to study catalysts containing aryl oxides of group 4 metals, in particular, those derived from sterically hindered phenols in ethylene polymerization. Early transition-metal complexes with chelating phenolate ligands hold promise as possible precursors in olefin polymerization as evidenced by recent trends.[13–17]

Most of the reported aryl oxides described by the formulation $(OR)_nMX_{4-n}$ [where R is the substituted phenol, X is the labile ligand, and M is Ti(IV) or Zr(IV)] are relatively ineffective in the presence of MAO as a cocatalyst in the production of low-molecular-weight PE.[1,18–22] In a previous work, we showed that under optimum conditions, it is possible to oligomerize ethylene to linear α-olefins with Ti(IV) aryloxo complexes of monodentate phenols of the type $M(OR)_4$ in the presence of alkyl aluminum halide cocatalysts other than MAO.[23] Subsequently, in a recent article, we reported for the first time that titanium (Ti) complexes of 1,1′-bi-2-aryl oxide, such as 1,1′-binaphthalene 2,2′-diol, which is an important $c_2$ symmetric chiral auxiliary ligand, promoted the polymerization of ethylene to a predominantly low-molecular-weight product having a high crystallinity and narrow PD.[24] To gain further insight into the interesting behavior of biaryloxy chelates of Ti(IV) in polymerization, in this study, a broad group of catalyst precursors containing sterically crowded biphenols were prepared and evaluated for catalytic ethylene polymerization in combination with ethylaluminum sesquichloride (EASC or $Et_3Al_2Cl_3$) as a cocatalyst. The steric effects of the substituents and the nature of the bridge at the 1,1′ position of the biphenols on the productivity of the PE wax with desired molecular characteristics was also studied under different reaction conditions.

## EXPERIMENTAL

### Materials

All work involving air and/or moisture-sensitive compounds was carried out with standard high-vacuum Schlenk or dry box (VAC) techniques. Toluene was refluxed over a sodium wire for 4 h and was distilled before use. Polymer-grade ethylene was used directly from a commercial plant, the pressure of which was adjusted with a two-stage regulator. Cocatalysts were purchased from Ethyl Corp. (Baton Rouge, LA) or Witco GmbH (Bergkamen, Germany) and were used without further purification. Titanium tetraisopropoxide and the different biphenols were purchased from Aldrich (Milwaukee, WI) an were used without further purification.

### Measurements

Microanalysis was carried out on a PerkinElme model 2400 instrument. The Ti content in the cat lysts was determined gravimetrically as $TiO_2$. A Pe kinElmer Fourier transform infrared spectromet (model Spectrum BX) was used to obtain IR spectr of samples pressed into KBr pellets over the 4000 400-$cm^{-1}$ range. The $^1$H-NMR spectra of the catalys were recorded in $CDCl_3$ solvent on a Varian NM 300-MHz spectrometer with tetramethylsilane as a internal reference. FAB mass spectral analysis of ca alysts was carried out on a Jeol SX 102/DA-60( mass spectrometer/data system with argon/xenc as the FAB gas. The accelerated voltage was 10 k and the spectra were recorded at room temperatur *m*-Nitrobenzyl alcohol was used as the matri Molecular weights of the polymers were determine with size exclusion chromatography. The high-ten perature gel permeation chromatography (GP( analysis of the polymers was carried out with Pol mer Lab's PL-GPC 220 chromatograph. A set three PL Gel Mixed B columns were used. 1,2,4-T chlorobenzene was used as the mobile phase 135°C. Irganox (0.0125%) was added to the mobi phase before filtration. A sample preparation un PL-SP260, was used to dissolve and filter the sar ples at 135°C. Solutions (0.2%) were injected wi the help of an autosampler to record the chromat gram. Viscotek's Trisec conventional software w used to analyze the chromatograms, which we matched with polystyrene calibration curves. Tl following MHK constants were used to constru a universal calibration curve. For polystyrene, $= 1.2105e^{-4}$ and $a = 707$; for PE, $K = 4.055e^{-4}$ and $= 725$. Differential scanning calorimetry (DSC) w performed under a continuous nitrogen purge on Mettler-Toledo DSC 822 instrument from 30 to 200 at a scanning rate of 10°C/min. Indium was used perform the calibration. Thermogravimetric anal sis/differential thermal analysis of the catalysts w recorded in air (heating rate = 10°C/min) from a bient temperature to 600°C on a TA Instrume (Universal V2). The density of the polymers w determined in an *n*-butyl acetate medium at 23°C per ASTM D 792-00. X-ray experiments were carri out on a Brüker AXS model D8 advanced diffr tometer. Scattering patterns were obtained with N filled Cu Kα radiation (λ = 1.5406 Å, generator vc age = 45 kV, current = 40 μA) in the reflection mo as detected by a scintillation counter. Samples we pressed films approximately 400 μ thick and we scanned into 2θ ranges from 15 to 45° at a rate of 1 min. Measurements were recorded at steps of 0.0

Scanning electron micrographs of powdered polymer samples were taken on a Jeol JFC 1100 instrument ion sputter water. They were observed in a Jeol 5600 CV scanning electron microscope in Hv mode at an operating voltage of 20 kV.

### Catalyst preparation

Catalysts 1–5 were synthesized by a modified literature procedure.[25] To a solution of 1 mmol (284.3 mg) of $Ti(OPr^i)_4$ in toluene (25 mL) was added slowly 1 mmol (186.2 mg) of the corresponding biphenol ligand in warm toluene (30 mL) under a nitrogen atmosphere; this mixture was heated at 60°C for 3 h. The contents were then stirred for 24 h at room temperature. The solvent was carefully removed, the precipitated solid was washed with small portions of warm toluene, and finally, orange complexes were isolated.

ANAL. Calcd for catalyst 1 ($C_{18}H_{22}O_4Ti$); C, 61.7%; H, 6.3%; Ti, 13.7%. Found: C, 60.5%; H, 6.6%; Ti, 13.2%. $^1$H-NMR ($CDCl_3$, 300 MHz): 6.96–7.33 (8H aromatic protons), 1.16 (12H, $CHMe_2$), 3.97 (2H, $CHMe_2$).

ANAL. Calcd for catalyst 2 ($C_{27}H_{28}O_4Ti$); C, 69.8%; H, 6.1%; Ti, 10.3%. Found: C, 69.2%; H, 6.1%; Ti, 13.0%. $^1$H-NMR: 6.87–7.83 (12H, aromatic protons), 1.19 (12H, $CHMe_2$), 3.91 (2H, $CHMe_2$), 4.48 (2H, $CH_2$ bridge).

ANAL. Calcd for catalyst 3 ($C_{19}H_{22}O_4Cl_2Ti$); C, 52.7%; H, 5.1%; Ti, 11.1%. Found: C, 53.1%; H, 5.2%; Ti, 11.5%. $^1$H-NMR: 6.96–7.23 (6H, aromatic protons), 1.19 (12H, $CHMe_2$), 3.79 (2H, $CHMe_2$), 3.92(2H, $CH_2$ bridge).

ANAL. Calcd for catalyst 4 ($C_{31}H_{48}O_4Ti$): C, 69.9%; H, 9.1%; Ti, 9.0%. Found: C, 69.2%; H, 9.8%; Ti, 9.4%. $^1$H-NMR: 6.98–7.24 (4H, aromatic protons), 1.17 (12H, $CHMe_2$), 3.96 (2H, $CHMe_2$), 2.56 (4H, $CH_2Me$), 1.22 (6H, $CH_2Me$), 1.38(18H, $^t$Bu).

ANAL. Calcd for catalyst 5 ($C_{36}H_{58}O_4Ti$): C, 71.7%; H, 9.7%; Ti, 7.9%. Found: C, 72.1%; H, 9.3%; Ti, 7.6%. $^1$H-NMR: 7.13–7.49 (4H, aromatic protons), 1.18 (12H, $CHMe_2$), 3.50 (2H, $CHMe_2$), 4.20 (1H, CHMe), 1.67(3H, $CHMe$), 1.38(36H, $^t$Bu).

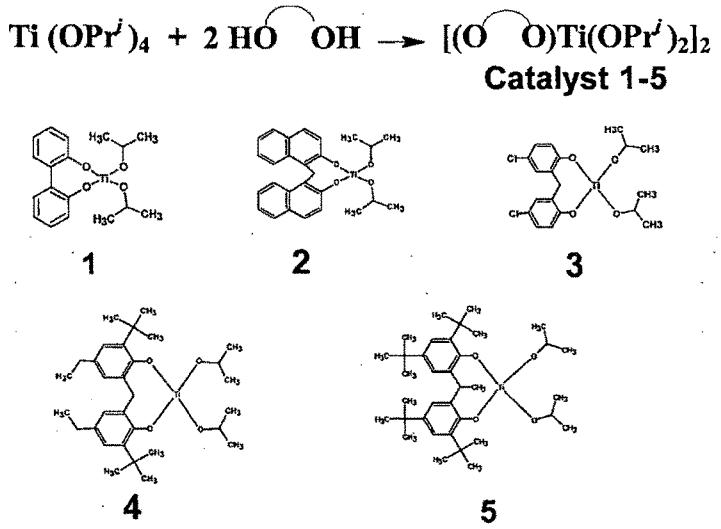
### Ethylene polymerization

Ethylene polymerization was conducted in a 600 mL-stirred autoclave (Parr) connected to a model 4850 microprocessor controller. Before polymerization, the reactor was heated to 150°C under nitrogen for 2 h and cooled to ambient temperature. In a typical experiment, catalyst 1 (10.3 mg, 0.029 mmol) dissolved in 50 mL of toluene and EASC (1.32 mL, 5.8 mmol) in toluene (200 mL) were carefully charged into the reactor under a nitrogen blanket. The Al/Ti molar ratio was 200. The reactor temperature was kept at 100°C and then pressurized with ethylene to 300 psi. The reaction was continued for 1 h, cooled, and degassed, and the slurry was slowly poured into acidic methanol (5%, v/v) to precipitate the polymer. The white PE powder was filtered, washed several times with methanol followed by acetone, and finally dried under reduced pressure at 70°C for 2 h.

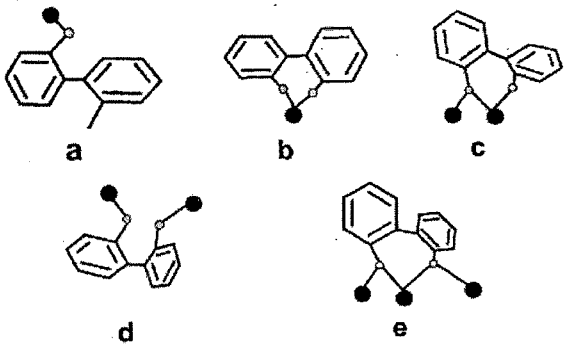
## RESULTS AND DISCUSSION

### Synthesis of Ti(IV) complexes with biphenol and its derivatives

The preparation of Ti–biphenolate complexes (1–5; Scheme 1) was accomplished by a stoichiometric reac-




**Scheme 1** (1) o—o = biphenol, (2) o—o = 1,1′-methylenedi-2-naphthol, (3) o—o = 2,2′ methylene bis(4-chlorophenol), (4) o—o = 2,2′ methylenebis(6-*tert*-butyl-4-ethyl phenol), and (5) o—o = 2,2′ ethylidene bis(4,6-di-*tert*-butyl phenol).




**Scheme 2** Coordination modes of the 2,2′-biphenolate ligand : (a) monodentate mode, (b) chelate (O,O′) mode, (c) bridging chelate (O,O,O′) mode, (d) bridging $\mu_2$ (O,O′) mode, and (e) doubly bridging chelate $\mu_3$ (O,O,O′,O′) mode.

tion between titanium tetraisopropoxide and a biphenol ligand (alcohol exchange) and the separation of liberated isopropanol by (azeotropic/vacuum distillation). This method was preferred over other reported ones[25(b)] as it proved convenient for working with toluene as a solvent for the polymerization of ethylene.

### Catalyst characterization

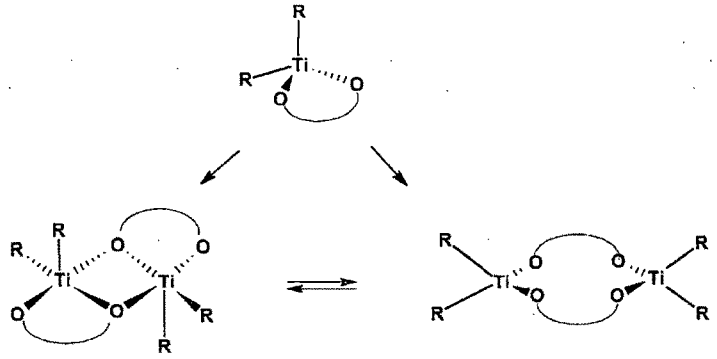
The stoichiometric reaction between $Ti(OPr^i)_4$ and biphenol ligand in toluene solution afforded dark orange complexes. All of the complexes described by the empirical formulation $Ti(Biphenol)(OPr^i)_2$ were soluble in aromatic solvents but only sparingly so in aliphatic hydrocarbons. Theoretically, the unsubstituted biphenol ligand could bind to Ti in at least five different ways, as shown in Scheme 2.

However, the most abundantly formed complexes were those with biphenol in the chelating mode [Scheme 2(b)] and, to a lesser extent, the bridging chelate mode [Scheme 2(c)].[26] In the absence of other ligands, the Lewis acidity of the titanates was enhanced greatly so that coordinative unsaturation was overcome by the formation of aggregates Depending on the molar ratio of the starting $Ti(OPr^i)$ and the biphenol derivative, a variety of complexe were previously isolated by Heppert, Walsh, an coworkers[27,28] but only a limited number of whic were characterized by X-ray crystal structure analysis Catalysts of type 1 were shown to exist as a dimer i the solid state based on X-ray analysis.[29] Thus, for ca alyst 1, we envisaged that the monomeric Ti(O—C $(OPr^i)_2$ could undergo facile intermolecular or intra molecular exchange in solution to produce dimeri forms, as indicated by the equilibria shown in Schem 3 between the two types of species.[30]

With increasing steric bulk of the biphenolat ligands, the tendency to form higher aggregates i the solid diminished. Such phenomena have prev ously been observed in other Ti–diolate catalysts.[31]

Catalysts 1–5 were characterized by microanalysis IR, $^1$H-NMR, FAB mass spectroscopy, and therm analysis. In a typical IR spectra of catalyst 1 and th corresponding biphenol, the low intensity broa peaks in the 3000–3500-$cm^{-1}$ region indicated depr tonation of the biphenolate ligand. The $^1$H-NMR spe tra were generally simple and were primarily used a a diagnostic tool to ascertain the purity of complexe A set of multiplets in the region 7.5–8.5 ppm for th aromatic protons was a common feature; in additio signals due to methyl protons of isopropyl grou (1–1.2 ppm) were observed. In the FAB mass spectr of catalyst 1, a prominent peak for a ligand fragme (biphenolate ion) appeared at 186. However, the pa ent ion was not detected, but the highest observe molecular weight ion at 308 was assigned to th $Ti(Biphenol)(OPr^i)^+$ species, which corresponded t the parent ion minus a coordinated alkoxide.[27(a),32]

In general, the higher stability of these catalysts wa apparent from the thermal degradation profile, whic indicated a single degradation peak around 480° assigned to the partial loss of the bulky biphen ligand. However, complete degradation to the dioxid $TiO_2$, was not noted up to 600°C for this catalyst.




**Scheme 3** Possible solid state equilibria in the catalyst.

**TABLE I**
**Ethylene Polymerization with the Ti–Biphenolate–EASC Catalyst Systems**

| Entry | Catalyst | Activity (kg of PE/g of Ti) | $M_w$ | PD | $T_m$ (°C) | $d$ (g/cc) |
|---|---|---|---|---|---|---|
| 1 | 1 | 11.4 | 1280 | 1.5 | 123.4 | 0.966 |
| 2 | 2 | 4.2 | 3380 | 1.9 | 129.1 | 0.954 |
| 3 | 3 | 7.8 | 1900 | 1.7 | 124.9 | 0.955 |
| 4 | 4 | 3.5 | 770 | 1.3 | 110.6 | 0.960 |
| 5 | 5 | 11.0 | 1760 | 1.5 | 125.6 | 0.953 |
| 6 | $Cp_2TiCl_2$ | 0.22 | — | — | — | — |
| 7 | $Cp_2ZrCl_2$ | 0.93 | — | — | — | — |

All reactions were carried out in a 600-mL SS reactor at 100°C and with 300 psi of ethylene pressure for 1 h.

### Polymerization of ethylene

The results of ethylene polymerization with catalyst precursors 1–5 are shown in Table I. The efficiency of the catalysts was compared with the known metallocene catalysts $Cp_2TiCl_2$ and $Cp_2ZrCl_2$ in the presence of EASC as a cocatalyst. The polymerization was carried out under different reaction conditions, including variations in temperature, Al/Ti ratio, pressure, solvent, and cocatalyst. Our initial examination of the catalysts indicated that among the different biphenols, the Ti complexes of 2,2′biphenol (catalyst 1) and ethylidene bis-2,4-di-*tert*-butyl phenol (catalyst 5) generally displayed higher activities in polymerization. The metallocenes, on the other hand, were practically inactive under these reaction conditions (Table I, entries 6 and 7). The activity was also predominantly dependent on the nature of the cocatalyst. EASC uniquely favored the polymerization. Other chlorinated alkyl aluminums, diethylaluminum chloride (DEAC or $Et_2AlCl$) and ethylaluminum dichloride (EADC or $EtAlCl_2$), were also active but with decreasing productivities. This rather exclusive combination of the Ti–diolate precursor and EASC cocatalyst in the polymerization suggested the formation of active intermediates responsible for polymerization, as discussed in the following section. Interestingly, the conventional cocatalysts for polyolefin production, including MAO and triethyl aluminum (TEAL or $Et_3Al$), showed poor activity with the isolated PE being largely coarse and inhomogeneous (Table II). A noteworthy feature of the PE obtained with these Ti–biphenolate catalysts was the invariably low molecular weight ($M_w$) of the polymers, as revealed by GPC analysis. In all cases, the PEs displayed narrow molecular weight distributions ($M_w/M_n$ = 1.3–1.9). However, monosubstituted tetra-aryloxides of Ti, such as $Ti(OR)_4$, essentially lead to low-molecular-weight linear α-olefins in the $C_4$–$C_{20}$ carbon range, in sharp contrast to the exclusive formation of solid PE with sterically bulky bidentate $Ti(O\text{^}O)_2$ type complexes used in this study.[23] This can be qualitatively interpreted as chain propagation rates of $r_p \cong r_t$ in the case of the $Ti(OR)_4$–EASC catalyst system, which resulted in oligomer formation, whereas with the $Ti(O\text{^}O)_2$–EASC system, $r_p > r_t$, which gave PE under identical conditions. The absence of ethylene oligomers in the solution was also confirmed by gas chromatography at the end of the reaction. Detailed studies on the effect of temperature and pressure were then carried out with complex 1 and EASC as the cocatalyst. From the results summarized in Table III, it was evident that increasing the reaction temperature from ambient to 100°C had a marked effect on the activity, as seen by about a 10-fold increase in the polymer yield (Table III, entries 1 and 3). A further increase in the reaction temperature (140°C), however, showed a marginal drop in productivity (entry 4). The effects of ethylene pressure are compiled in Table IV. Optimum pressure for good activity was around 300 psi at 100°C and at a Al/Ti ratio of 200 (Table IV). Applying higher pressure under similar conditions led to a higher productivity. Generally, a combination of a higher Al/Ti ratio and a higher temperature led to improvement in the productivity of the catalyst.

**TABLE II**
**Effect of the Cocatalysts on Ethylene Polymerization at 100°C**

| Entry | Cocatalyst[a] | Activity (kg of PE/g of Ti) | $T_m$ (°C) |
|---|---|---|---|
| 1 | EASC | 11.4 | 123.4 |
| 2 | DEAC | 6.6 | 127.4 |
| 3 | MAO | 2.0 | 132.4 |
| 4 | TEAL | 1.9 | 121.3 |
| 5 | EADC | 3.5 | 122.1 |

[a] Catalyst 1; $P_{C2H4}$ = 300 psi.

**TABLE III**
**Effect of the Temperature on Polymerization**

| Entry | Temperature (°C) | Activity (kg of PE/g of Ti) | $T_m$ (°C) |
|---|---|---|---|
| 1 | 30 | 1.2 | 131.1 |
| 2 | 60 | 2.9 | 128.6 |
| 3 | 100 | 11.4 | 123.4 |
| 4 | 140 | 10.2 | 124.8 |

Catalyst 1 EASC; $P_{C2H4}$ = 300 psi.

**TABLE IV**
**Effect of the Pressure on Ethylene Polymerization**

| Entry | $P_{C2H4}$ (psi) | Activity (kg of PE/g of Ti) | $T_m$ (°C) |
|---|---|---|---|
| 1 | 300 | 11.4 | 123.4 |
| 2 | 500 | 16.5 | 122.5 |

Catalyst 1 EASC; temperature = 100°C.

A brief examination of the effects of different solvents (Table V) indicated that chlorinated aromatic solvents, such as chlorobenzene, showed an increase of about 65% in the productivity of PE over that for toluene. Interestingly, this increase was accompanied by a twofold increase in $M_w$. However, aliphatic hydrocarbon solvents, such as hexane, resulted in poor activity, which may have been due to the low solubility of catalysts in these solvents.

To investigate the properties of PE waxes reported in Table I, they were characterized by GPC. In most cases, the major peak ($M_w$) was centered between 1.2–1.9 ($\times 10^2$). A commercial PE wax sample was also included as a reference for comparison. GPC of this material also displayed similar distribution in the low-molecular-weight region. As mentioned earlier, some of the striking features of these PE waxes were the exceptionally low molecular weights ($M_w$ = 770–3380) and narrow PDs (PD = 1.3–1.9). In no case was a high-molecular-weight PE ($\sim M_w \geq 10^5$) obtained, although these catalysts resembled typical Ziegler systems. As described in the Introduction, PE waxes with interesting applications have similar molecular weights and molecular weight distributions. DSC (Fig. 1) also revealed lower $T_m$ values than those observed for conventional high-density PE or low-density PE. As a benchmark for the comparison of polymer properties with those obtained in this study, a known sample of micronized PE wax was used. [The commercial samples used in this study, MPP123 and MPP635, were micronized, high-$T_m$, crystalline forms of polyethylenes, which were supplied by M/s Micro Powders, Inc. The products had $T_m$ values of 125–135°C, a molecular weight of 2000, $d$ (25°C) of 0.96, and a maximum particle size of 31 μm. These and other grades of PE waxes were designed to increase the abrasion resistance and antiblocking characteristics in flexographic inks and

**TABLE V**
**Influence of Solvent on Polymerization**

| Entry | Solvent | Activity (kg of PE/g of Ti) | $M_w$ | PD | $T_m$ (°C) |
|---|---|---|---|---|---|
| 1 | Hexane | 0.62 | — | — | — |
| 2 | Toluene | 11.4 | 1280 | 1.5 | 123.4 |
| 3 | Chlorobenzene | 18.8 | 2520 | 1.6 | 121.6 |

Catalyst 1 EASC; $P_{C2H4}$ = 300 psi.

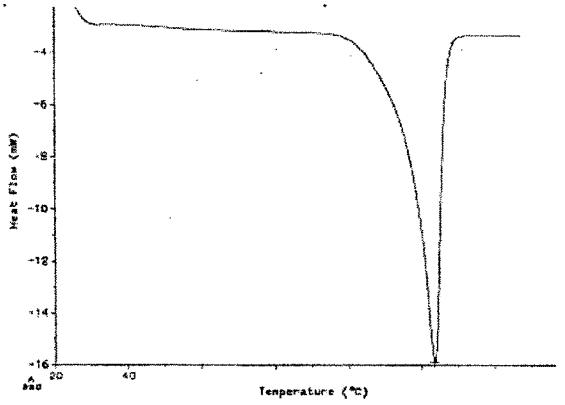



**Figure 1** DSC thermograms of the (a) PE wax and (t commercial sample (Table I, entry 1).

industrial paints and coatings. More details ar available at http://www.micropowders.com.]. Th intensity of the equatorial peaks in the X-ray diffrac togram (Fig. 2) for the 110 (2θ = 21.6°) and 200 (2 = 24°) reflection planes for the experimental sampl closely matched the intensity of the reference sam ple, and the pattern was indicative of orthorhomb crystallinity in these samples.

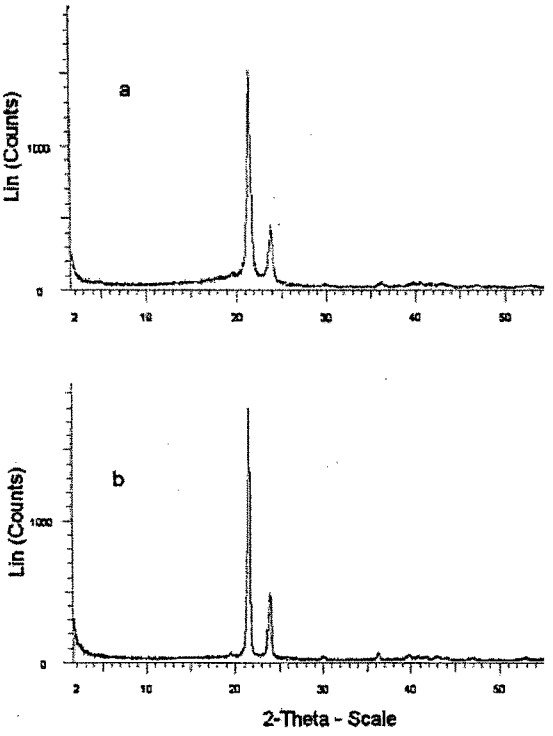
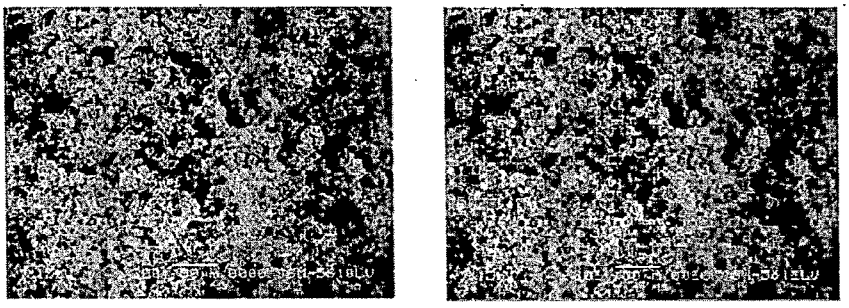



**Figure 2** X-ray diffractograms of the (a) PE wax (Table entry 1) and (b) commercial sample.



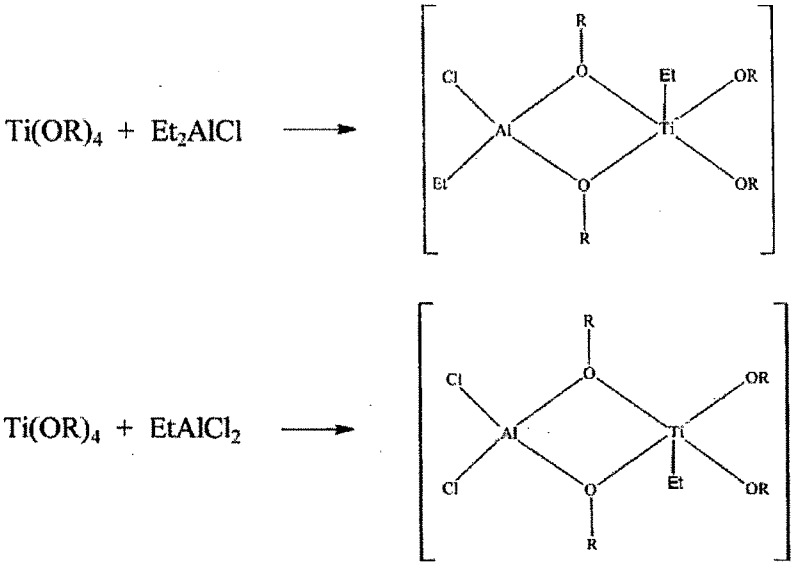
a b

**Figure 3** Scanning electron micrographs of the (a) PE wax (Table I, entry 1) and (b) commercial sample.

The crystalline nature of these polymers was also estimated by integration of the X-ray diffraction peaks observed for the wax samples. A high degree of crystallinity was indicated in all cases, which was generally in the range 70–83%. The polymer particles were fine and had a uniform morphology, as shown by scanning electron microscopy. A common feature of these waxes was that the average particle size of the polymer, as measured during the postreactor workup, was typically less than 400 μ. In Figure 3, comparative scanning electron micrographs for one of the samples obtained in this study and a commercial PE wax product are shown. The unique waxlike polymer obtained by these Ti–biphenolate–EASC catalyst systems could be fine-tuned to tailor the $M_w$ and PDs to the requirements of its end-use application.

### Catalytic pathway

Treatment of mononuclear $Ti(OR)_4$-type alkoxides with alkylaluminum halides has been reported to yield active intermediates (shown next) responsible for the polymerization of ethylene to low-molecular-weight products.[33,34]




We believe that a similar type of active species may have been involved in this Ti–biphenolate system. Moreover, as EASC was derived from an equimolar mixture of EADC and DEAC,[35] we have

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

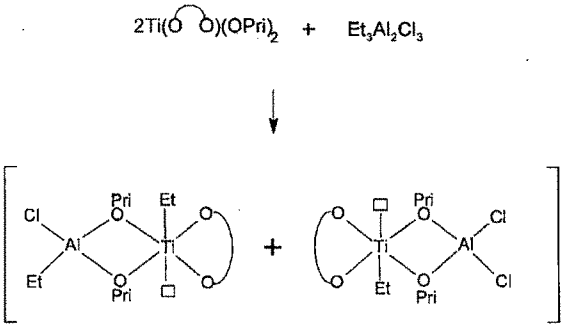
Because EASC could dissociate as DEAC and EADC in solution, it was reasonable to expect the formation

of two types of catalytic species on interaction with the Ti–biphenolate catalyst. The reduction of Ti(IV) in the presence of EASC would generate catalytically active components. As shown in Scheme 4, the active catalysts in the polymerization needed to retain a monomeric four- or five-coordinate geometry to allow for olefin insertion and subsequent propagation.[36] In this Ti–biphenolate catalytic system, higher temperatures tended to favor the formation of active intermediates responsible for polymerization.

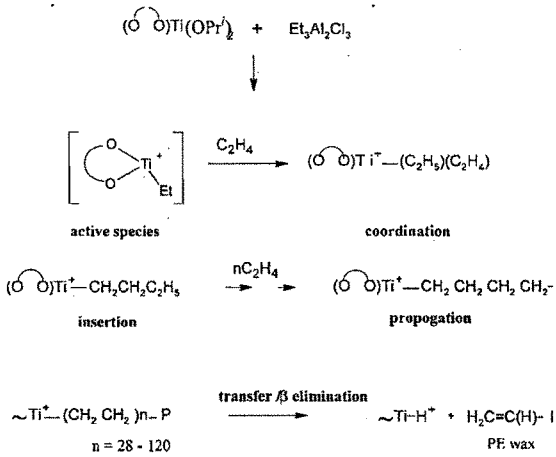
### Mechanistic aspect

On the basis of a theoretical study by Morokuma and coworkers[37] on the catalytic polymerization by chelating bridged and nonbridged titanium aryloxides, we propose that a similar mechanistic pathway (Scheme 5) was operative in this Ti–biphenolate–EASC catalytic system.[38,39] Although the identity of active cationic species remained elusive, their possible involvement was postulated through *in situ* UV–visible spectral studies. In our system, the initial absorption band at about 360 nm for the catalyst precursor 1 with EASC showed a distinct shift to higher wave numbers ($\lambda_{max} \sim$ 420 nm, LMCT) in the presence of ethylene, which indicated the formation of a transient Ti–alkyl intermediate. Similar spectral behavior was also noted by Kaminsky[40] for polymerization catalysts containing Ti(IV) metallocenes and MAO.

Although chain transfer can occur by other reactions as well, the relative inactivity of these catalysts with MAO and TEAL indicated that termination was unlikely to proceed by transfer to Al–alkyl or by $H_2$ under the reaction conditions. It was obvious that steric factors in biphenols and the coordination geometry around the Ti atom contributed significantly toward productivity and *inter alia* molecular weight regulation. For example, in system 1 (direct bridge between phenolic groups), the calculated chelate O—Ti— O bite angle corresponded to 96.1°, whereas for the $CH_2$ bridged systems (2–4), it was around 103.4°, which led to a lower insertion barrier energy




**Scheme 4** Reaction of catalyst 1 with EASC.




**Scheme 5** Proposed mechanism of ethylene polymeriza tion by Ti–biphenolates.

for system 1 (10.7 kcal/mol).[37] Indeed, experimer tally, this effect was reflected in higher activities fc catalyst 1 compared to catalysts 2–4 (Table I). Inte estingly, catalyst 5 showed good activity an behaved similar to catalyst 1. Apparently, in th case, the situation was slightly different due to th extra methyl group in the bridge. Although the bi angle for this ligand was currently not available, it possible that there was an enhanced Ti–biphen bridge interaction in this particular case, as seen, fc instance, in sulfur bridged biphenols, which thereb favored higher activity due to alteration in the ene getics of the O—$C_{Me}$—O—Ti chelate.[41] Furthermor the polymer molecular weight was highly depende on the nature of the biphenol ligand within the cat lyst precursor. As the bulk of the ligand increase the polymer molecular weight increased (1200 fc catalyst 1 to 3400 for catalyst 2 and ca. 1800 for cat lysts 3 and 5). An exception appears to be catalyst which had an unusually lower $M_w$, although i activities were much lower than those of catalyst This trend, combined with the effect on productivi of the PE wax (Table I), implied that the ligands th generated the highest molecular weights did so b slowing β-hydrogen abstraction. Although the stru ture of active intermediates is as yet unknown, tl mechanism leading to these linear low-molecula weight PEs was consistent with those reported prev ously for solution-phase olefin polymerization wi titanium alkoxides and aluminum alkyls.[13,37] Efforts are underway to investigate the detail kinetics of this reaction.

## CONCLUSIONS

Complexes of Ti(IV) with sterically bulky biphenc acted as efficient catalysts in the presence of EASC

a cocatalyst for the synthesis of specialty low-molecular-weight PEs with good productivities. The catalyst activity was significantly influenced by the reaction temperature and Al/Ti ratios. The physical properties exhibited by these PEs, such as low molecular weights, high crystallinities, and narrow PDs, suggested the single-site catalytic behavior of these Ti–biphenolate precursors. The close resemblance of the polymer properties to those of commercially important synthetic waxes holds promise for the development of alternative, cheaper catalysts for this process.

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# Catalytic ring-opening polymerization of L-lactide by titanium biphenoxy-alkoxide initiators

P.S. Umare [a], G.L. Tembe [b,*], K.V. Rao [b], U.S. Satpathy [b], B. Trivedi [a]

[a] *Department of Chemistry, The M.S. University of Baroda, Vadodara 390 002, India*
[b] *Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India*

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**Abstract**

Six different titanium biphenolate complexes were synthesized and investigated as initiators for the ring opening polymerization of L-lactide in the bulk phase but typically below the degradation temperature of the monomer. All the titanium complexes are effective in forming polylactide with good conversions. The nature and steric bulk of the phenolic ligands coordinated to the central titanium greatly influence polymer properties. In all cases the PLA obtained display low molecular weights and narrow disperisities. Both $^{1}H$ and $^{13}C$ NMR spectra indicate the polymers to be essentially isotactic in nature. High crystallinity and controlled morphology of polylactides are uniquely different compared to conventional high molecular weight PLA obtained with tin based initiator.


*Keywords:* Poly(L-lactide); Ring-opening polymerization; Titanium biphenoxy-alkoxide catalysts

## 1. Introduction

One of the most extensively studied biodegradable polymers over the past two decades has been polylactide (PLA), which can be commercially obtained from renewable materials, such as corn, beet, dairy products, etc. [1]. The biocompatibility of PLA has found increasing application in medical, packaging, film and as thermoplastics [2]. These degradable polyesters can be synthesized either by polycondensation of lactic acid or from ring-opening polymerization (ROP) of the cyclic dimer, namely lactide [3]. The polycondensation route has inherent drawbacks like poor kinetic control and removal of liberated byproduct water which induces reverse reaction resulting in the hydrolysis of the ester linkages of polymer. Moreover, commercially prepared L-lactic acid by fermentation contains about 10 wt.% water (w/w) necessitating the use of water-tolerant catalysts for dehydropolymerization. Consequently, there exists a need for developing other methods for preparation of these degradable polymers in a reproducible fashion. Thus, a large number of Lewis acidic catalysts have been shown to facilitate the ROP of lactide allowing for better control over the molecular weights and molecular weight distributions. A review of literature suggests that compounds of tin, such as stannous octoate (Sn(II)-2-ethylhexanoate) and its derivatives are the most extensively studied for this reaction [4]. Other catalysts, such as aliphatic alkoxides of Al [5], Zn [6], Mg [7], carboxylates of Fe(II) [8], aryl oxides of lanthanides [9,10] and more recently examples of actinide complexes containing cyclopentadienyl ligand [11] have all been shown to promote polymerization of lactide but are relatively less effective. A common conclusion from these studies is that different catalysts lead to different kinds of PLAs with significant differences in molecular weights and MWD. One of the reasons for this is the effect of ester interchange and racemization that occurs under the polymerization conditions employed. Though a large number of metal alkoxide based initiators are capable of polymerizing LA, the search for new-catalysts remains actively pursued to generate polylactide with well-defined stereochemistry and precise control over physical properties for end use.

In view of the above it is rather surprising to note that application of initiators based on titanium in ROP of lactide is rather scanty though they have been demonstrated as potential catalysts for α-olefin polymerization [12]. Homogeneous catalysts based on titanium, such as $TiCl_x(OPr^i)_{4-x}$ [13], chalcogen-bridged

* Corresponding author. Tel.: +91 265 6696492; fax: +91 265 6693934.
*E-mail address:* gopal.tembe@ipcl.co.in (G.L. Tembe).

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bis-aryloxides of Ti [14], titanatranes [15] and amino-bisphenolate derivatives of titanium [16] have recently been investigated as catalysts for bulk and solution phase ring opening polymerization of *rac*, D,L- and L-lactide. Polymer properties varied widely depending on the ligating environment and method of polymerization. As part of our current interest in the application biphenolate compounds in ethylene polymerization it was found that Ti-BINOLates and analogues exhibited unique activity in producing polyethylene with controlled molecular weights and microstructure [17,18]. The versatility associated with these Ti-compounds and their ability to promote controlled olefin polymerization prompted us to explore them further as initiators for L-lactide polymerization. In the present work, we describe our results on the activity of alkoxy-biphenolate family of titanium catalysts and examine in detail the properties of polylactides obtained *via* ROP. The strategy employed is based on selecting catalysts of the form $L_nTi(OR)_{n-4}$, where OR is the alkoxide that is readily capable of propagating the polymerization and $L_n$ is an end capped bulky biphenol.

## 2. Experimental

### 2.1. Materials

L-Lactide was synthesized from commercial L-(+)lactic acid (>99%, Fluka) and was purified by repeated crystallization and drying under vaccum at 70–75 °C for 2–3 h. The optical purity of the monomer was >98%.

### 2.2. Catalyst preparation

The catalysts **1–5** were prepared by an alcohol exchange method by reacting $Ti(OPr^i)_4$ and the corresponding biphenols. The synthetic protocol and details of characterization have been described in a previous publication [17,18]. The pre-dried complexes were then used in the melt and solution polymerization of lactide as described below.

### 2.3. Polymerization

LA bulk polymerization was carried out by charging 1 g of LA and then the appropriate amount of catalyst precursor to 50 ml Schlenk flask. The flask was then immersed in the oil bath at 130 °C for specified time. The reaction was terminated by the addition of 5 ml of methanol. The precipitated polymer were dissolved in a minimum amount of methylene chloride and then excess methanol was added The resulting reprecipitated polymer was collected, washed with 3× 50 ml of methanol and dried in vacuum at 50 °C for 12 h.

### 2.4. Polymerization of L-LA by Sn(II)-2-ethylhexanoate

Melt polymerization was carried out at 180 °C for 1 h. After cooling the melt was dissolved in chloroform and precipitated from methanol. The dried white coloured PLA was fibrous in nature.

Solution polymerizations of LA were carried out in a 50 ml Schlenk flask using toluene as a solvent.

### 2.5. Measurements

Elemental analyses 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 $^1H$ and $^{13}C$ NMR spectrum of polylactides was recorded in $CDCl_3$ and DMSO-$d_6$ solvent on a Varian NMR 300 MHz spectrometer using TMS as an internal reference.

Molecular weights of polymers were determined using size exclusion chromatography (SEC). The GPC analysis of the polymers was carried out using Perkin-Elmer, Series-200 chromatograph. A set of PL Gel 5 μm $10^4$ Å (300 mm × 7.5 mm) column was used. Tetrahydrofuran (THF) was used as the mobile phase at 30 °C. Differential scanning calorimetry was performed under a continuous nitrogen purge on a Mettler-Toledo DSC 822 instrument from 50 to 220 °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). 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 and 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 13° to 45° at a rate 1°/min. Measurements were recorded at steps of 0.02°. Scanning electron micrographs of powdered polymer samples were taken on a JEOL JFC 1100 instrument ion sputter water. They were observed in JEOL 5600 CV Scanning Electron Microscope in Hv mode with operating voltage of 20 kV.

## 3. Results and discussion

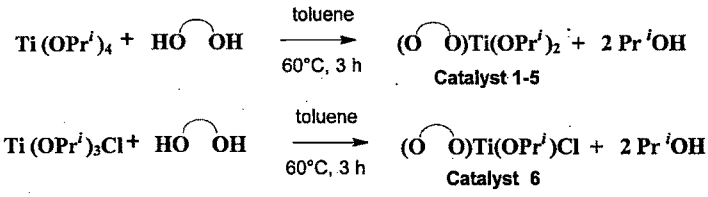
### 3.1. Synthesis of titanium catalysts

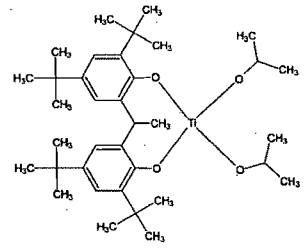
The catalysts chosen for the lactide polymerization contain isopropoxide groups along with bulky biphenols attached to titanium. Thus, the complexes were obtained by direct reaction of $Ti(OPr^i)_4$ or $Ti(OPr^i)_3Cl$ and the corresponding phenol as outlined in Scheme 1.

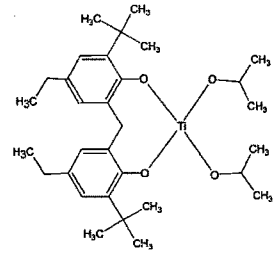
The liberated isopropanol was separated by repeated washing of catalyst and followed by azeotropic distillation. In order to have proper comparison of activity levels of all catalysts, the starting $Ti(OPr^i)_4$ complex was also evaluated along with catalysts **1–6**. Moreover, since it is known that polylactide properties depend to a great extent on the nature of initiator a known lactide polymerization catalyst Sn(II) octoate was also included as reference to ensure reliable comparison of data.

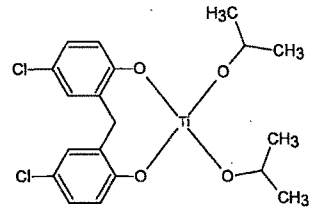
### 3.2. Bulk polymerization

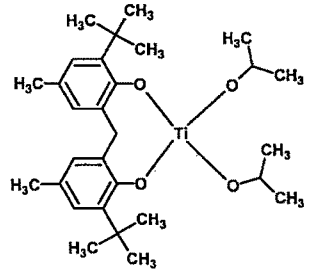
The different (isopropoxy)-titanium biphenolates **1–6** were employed as catalysts to initiate ring opening polymerization of

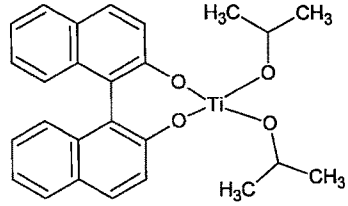


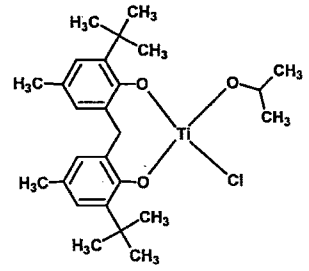


Catalyst 1


Catalyst 2


Catalyst 3


Catalyst 4


Catalyst 5


Catalyst 6

Scheme 1. Synthesis of Ti catalysts.

neat L-lactide by carefully heating the thoroughly mixed components under inert atmosphere at 130 °C. The initiation of lactide polymerization was visually indicated when the temperature of the mixture reached 110 °C accompanied by a distinct colour change of the melt to dark-brown viscous mass in case of titanium catalysts. For the Sn(II) catalyst the colour change was not apparent but a change of viscosity was clearly noticed.

For the titanium catalyst containing biphenols simple precipitation of the polylactide powder from methanolic solution lead to polymers having light brown to pale yellow colouration. Repeated reprecipitation was found essential to decolourize the polymers to acceptable levels for further characterization. We aimed at unraveling the effect of bulky biphenolate ligand and the nature of substituent on the ROP of L-lactides. All the Ti-catalysts gave polymers which were very fine powders. In Table 1 is compiled the results of polymerization of L-lactide with different catalysts.

The observed molecular weights based on GPC with catalysts **1–6** are below $1 \times 10^4$. This is in sharp contrast to very high molecular weights typically obtainable by tin compounds. An increase of polymerization temperature from 130 to 180 °C while maintaining other parameters same showed a marked increase of polymer molecular weight as is evident (Table 1, entries 1 and 8) for catalyst **1**. Similarly the reaction time also showed a positive effect on overall conversion of lactide (Table 1, entry 7). On the other hand, the influence of biphenolate ligand or the linkage/substituent on the phenyl ring did not show any specific trend on molecular weights of polymer. However, the narrow molecular weight distribution in most cases suggest the presence of single site catalyst. Nevertheless the low molecular weights and higher crystallinity are rather unique to these mixed alkoxy-biphenolate catalysts [19]. Interestingly the reference polylactide based on Sn(II) octoate showed presence of higher contents of amorphous materials (Table 1, entry 12). The comparison of variation in PLA properties in presence of titanium isopropoxide initiator under different reaction conditions is shown in Table 2. The results indicate that the Ti(OPr$^i$)$_4$ acts as a living ring opening polymerization catalyst. Alkoxy titanium(IV) complexes containing chelating tetradentate dianionic phenolate ligands [Ti(ONNO)(OPr$^i$)$_2$] exhibited lower activity requiring extended reaction times, typically 20–50 h. Similarly alkoxy-titanatrane catalysts of the type Ti(OOON)(OPr$^i$)$_2$ displayed higher $M_w/M_n$ values (1.8–2.2) than the present biphenolate based complexes [14,15]. These results lead us to infer that control of polymerization is much better with bidentate biphenolate type of ligands as revealed by PDI between 1.3 and 1.6.

Table 1
L-Lactide polymerization with titanium biphenoxy-alkoxide initiators[a]

| Entry | Catalyst | Time (h) | Temperature (°C) | Yield (%) | $M_w$ | $M_n$ | PD | $T_m$ (°C) | $X_c$ (%) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | XRD | D |
| 1 | 1 | 2 | 130 | 96 | 6,760 | 4,400 | 1.5 | 130 | 51 | 4 |
| 2[a] | 5 | 2 | 130 | 95 | 9,170 | 5,500 | 1.5 | 130 | 47 | 4 |
| 3[a] | 2 | 2 | 130 | 87 | 6,300 | 3,990 | 1.6 | 126 | 50 | 4 |
| 4[a] | 4 | 2 | 130 | 81 | 6,220 | 3,930 | 1.5 | 130 | 53 | 5 |
| 5[a] | 3 | 2 | 130 | 67 | – | – | – | – | – | – |
| 6[a] | 6 | 2 | 130 | 33 | 4,670 | 3,170 | 1.5 | – | – | – |
| 7 | 1 | 8 | 130 | 96 | 8,560 | 5,035 | 1.7 | – | – | – |
| 8[a] | 1 | 2 | 180 | 95 | 14,470 | 8,330 | 1.7 | 133 | 52 | 4 |
| 9[b] | 1 | 12 | 80 | 00 | – | – | – | – | – | – |
| 10[b] | 2 | 12 | 80 | 00 | – | – | – | – | – | – |
| 11[a] | $Ti(OPr^i)_4$ | 2 | 130 | 94 | 6,300 | 4,150 | 1.5 | 131 | 52 | – |
| 12[b] | Sn (octoate) | 1 | 180 | 98 | 108,000 | 52,110 | 2.1 | – | – | – |
| 13[c] | $Ti(OPr^i)_4$ | 12 | 200 | – | 19,800 | 10,400 | 1.9 | 144 | – | 4 |

[a] [LA]/[Ti] = 300.
[b] [LA]/[Ti] = 1000.
[c] Ref. [26].

Table 2
Comparison of polymer properties derived from $Ti(OPr^i)_4$

| Entry | Catalyst | Time (h) | Temp (°C) | Yield (%) | $M_w$ | $M_n$ | PD | $T_m$ (°C) | $X_c$ (%) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | | | | | XRD | D |
| 1 | $Ti(OPr^i)_4$ | 2 | 130 | 94 | 6,300 | 4,150 | 1.5 | 131 | 52 | |
| 2[a] | $Ti(OPr^i)_4$ | 2 | 130 | 75 | 35,700 | 16,000 | 2.2 | – | – | |
| 3[a] | $Ti(OPr^i)_4$ | 0.5 | 130 | 20 | – | – | – | – | – | |
| 4[b] | $Ti(OPr^i)_4$ | 12 | 180 | – | 12,000 | 6,600 | 1.8 | 151 | – | 4 |

[a] Ref. [13].
[b] Ref. [26].

### 3.3. Solution polymerization

Our efforts to synthesize polylactide by reacting the monomer and the catalysts **1–6** in toluene solutions were unsuccessful (Table 1, entries 9–10) under the conditions employed (80–100 °C). In all cases the initial light-yellow/orange colour of the solution remained unchanged. It is possible that the formation of dimeric or higher agglomerates involving titanium isopropoxy bridges may preclude the insertion/interaction of the monomer and facilitate propagation. This aspect was investigated further.

### 3.4. Polymer characterization

Polylactides obtained with titanium biphenoxy isoprox catalysts at 130 °C generally showed lower molecular mass revealed by GPC (Figs. 1 and 2). At the given temperat regardless of the type of chelating biphenol attached to titani

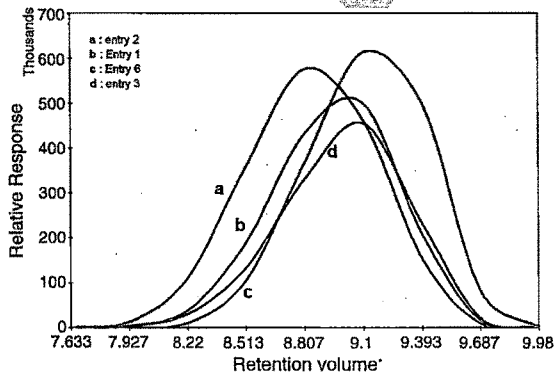



Fig. 1. GPC profiles of L-PLA: Table 1, (a) entry 2, (b) entry 1, (c) entry 6 and (d) entry 3.

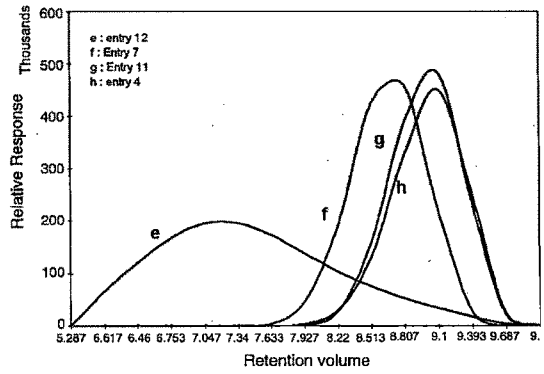



Fig. 2. GPC profiles of L-PLA: Table 1, (e) entry 12, (f) entry 7, (g) entr and (h) entry 4.

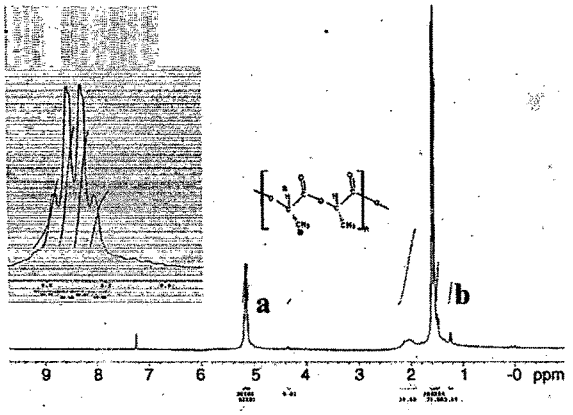



Fig. 3. $^1$H NMR of L-PLA: Table 1, entry 1.

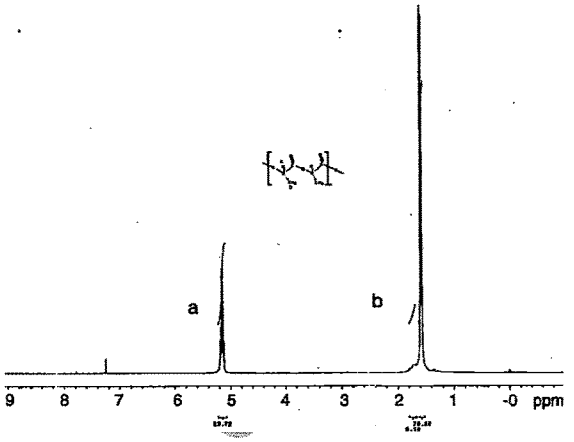



Fig. 4. $^1$H NMR of L-PLA: Table 1, entry 12.

the variations in MWD are only marginal and the peak $M_w$ values centered around $0.6 \times 10^4$. Increase in reaction temperature for e.g., in case of **1** lead to an increase in $M_w$ to about $1.4 \times 10^4$ though the MWD showed only a slight increase. The polylactide prepared by Sn(II) complex displays $M_w$ in the range of $1.1 \times 10^5$, but PDI values are some what higher at 2.1.

Homonuclear decoupled $^1$H NMR as well as $^{13}$C NMR spectrum of the polylactides were recorded to elucidate the microstructure of both the low molecular and high molecular weight polymers synthesized using the Ti as well as the Sn catalyst. Depending on the stereochemical configuration three possible polymer types *viz.* isotactic, heterotactic or syndiotactic can be distinguished by the peak positions and nature of methine and methyl resonances in the spectra [4b]. The $^1$H NMR spectrum of PLA in (Figs. 3 and 4) reveals only two major sets of signals, namely the well resolved quartet of CH protons centered at $\delta \sim 5.1$ ppm and doublet for $CH_3$ protons at $\delta \sim 1.2$ ppm [20]. Such an absorption pattern is indicative of isotactic nature (-SSSS or -SSRR-stereosequence) of PLA. In the $^{13}$C NMR spectrum (Figs. 5 and 6), the peak appearing at ~169.7 ppm is due to the ester carbonyl group but there was no peak due to the free carboxylic end groups in the low field region. In the high field spectrum methine and methyl resonances appear at ~69.4 ppm and 17.3 ppm, respectively [21]. The pattern is nearly identical for both the Ti as well as Sn(II) initiators indicating that the same stereochemical sequence is present in the polymers derived from these catalysts, though the molecular weights differ widely. The absence of carboxylic resonance may indicate possibility of formation of macrocylic oligomers. However, the proportion of this lactide may be minimum as the $M_n$ values obtained by GPC are generally well above $0.5 \times 10^4$. Moreover, cyclization would require extensive intramolecular

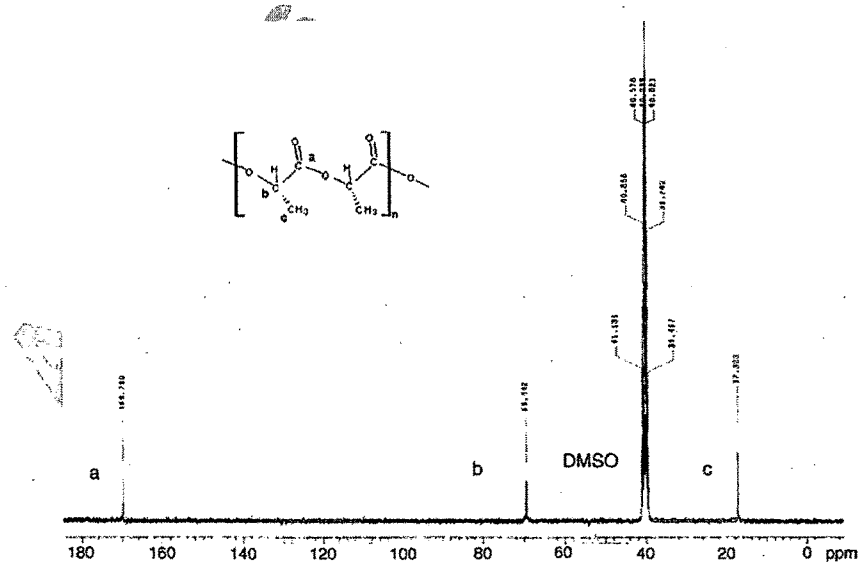



Fig. 5. $^{13}$C NMR of L-PLA: Table 1, entry 1.

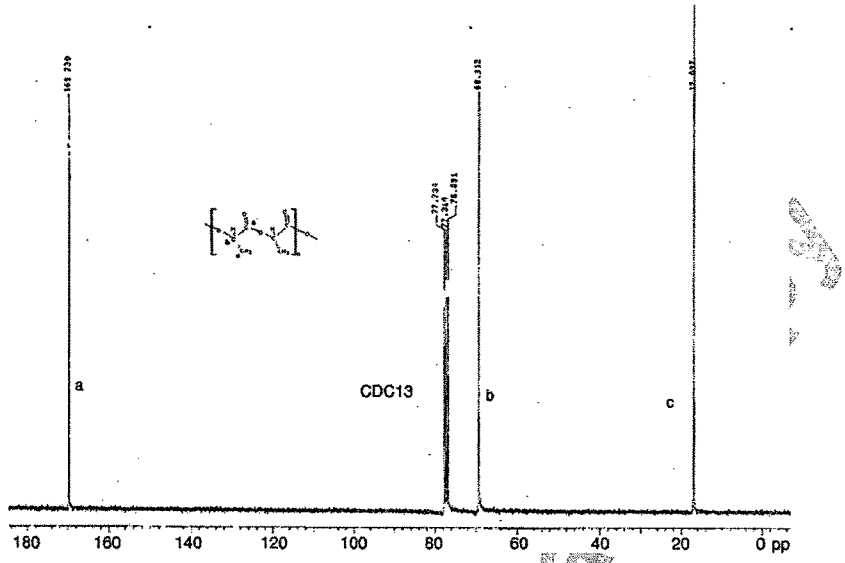



Fig. 6. $^{13}C$ NMR of L-PLA: Table 1, entry 12.

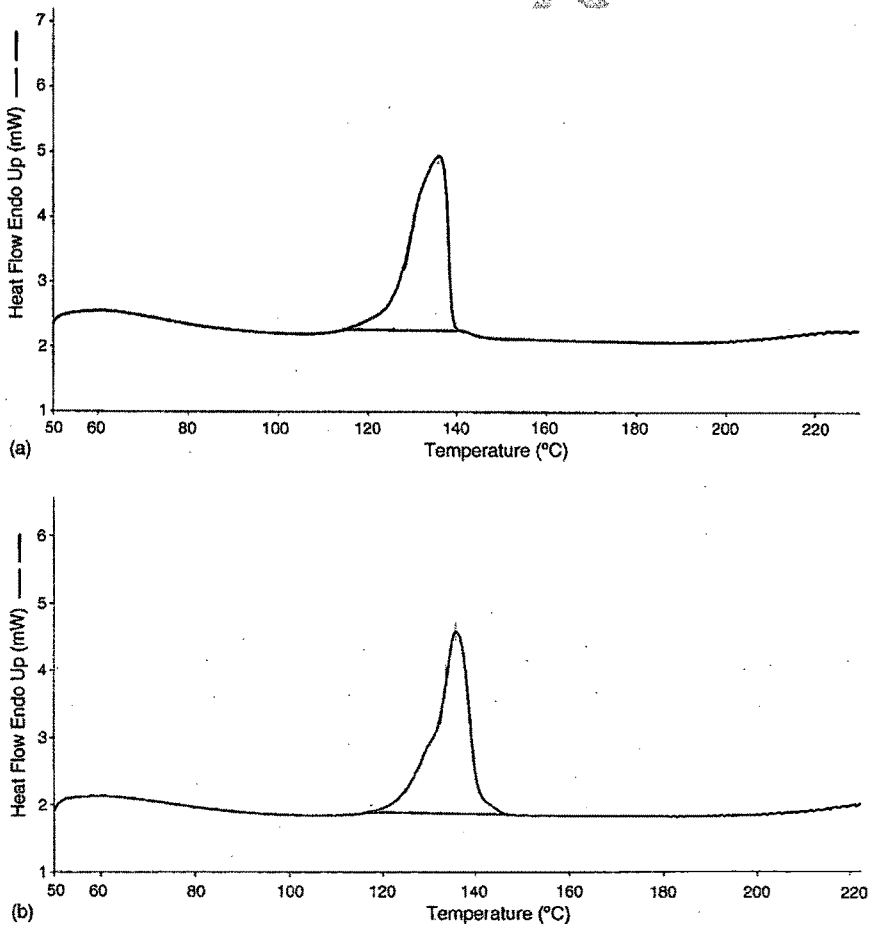



Fig. 7. Representative DSC of L-PLA: Table 1, (a) 1 and (b) 3.

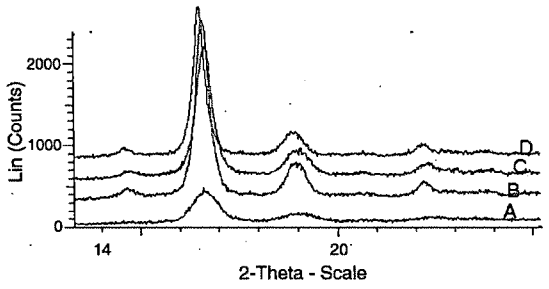



Fig. 8. XRD of L-PLA: Table 1, (A) entry 12, (B) entry 1, (C) entry 2 and (D) entry 3.

transesterification involving long post-polymerization periods. Similar phenomena have been noted earlier for ROP of cyclic esters by other initiators [22,23]. Since polymerization is likely to proceed *via* coordination—insertion mechanism it is necessary to check for possible end groups in the isolated polymer. Weak signals due to isopropoxy methyl groups were noticed at $\delta \sim 1$ ppm [20] consistent with the above polymerization process. However, resonance due to hydroxy protons were not easy to assign. We believe that one of the ester end groups of PLA may be strongly bound to Ti-catalyst residues. Absence of any other signals in $^{13}C$ NMR also suggests that effects of trans-esterification or racemization may be insignificant [4a,24,25].

The semi-crystalline nature of all the polylactides was confirmed by percentage crystallinity obtained by the endothermic peak in the DSC (Fig. 7). In all the PLAs prepared by the Ti-catalysts $X_c$ values are around 50% which is by far the highest than any of the previously achieved by titanium alkoxide based initiators [26]. The higher crystallinity (>40%) of PLAs in all cases resulted in no glass-transition temperature ($T_g$) to be observed while the $T_m$ values were in the range of 125–138 °C indicating semi crystalline nature of the polymer [13,26].

The DSC values were also consistent with the crystallinity results obtained by X-ray powder diffractogram (Fig. 8). The XRD reveal strong signals centered at $2\theta = 19°$ due to (2 2 0 plane, Bragg distance $d = 4.7$ Å) and another at $2\theta = 16.6°$ (2 0 0 plane, Bragg distance $d = 5.3$ Å). All these peaks correspond to the α form while the β form was not observed suggesting that the L-PLA exists in a single phase. Low intensity crystalline peaks (α form) were also observed at 14.6° and 22.3° in case of PLA synthesized by Ti complexes (Fig. 8B–D) whereas they are less pronounced in case of Sn(II) initiator (Fig. 8A) [27]. $X_c$ values obtained for PLA derived from Sn(II) octoate by DSC and XRD were around 35%. These variations are reflective of the subtle differences in Lewis acidic nature of Ti and Sn centers and their ligand environment. The scanning electron micrographs of PLAs (Fig. 9) reveal the polymer derived from Ti-catalysts to consist of loosely bound particles with smooth surface. In the case of the high molecular weight PLA obtained by Sn(II) catalyst the particles are less smooth but are seen as long strands attached to one another.

It is thus possible to tailor the catalyst in order to obtain PLAs with desired morphological features for end application. In the present PLAs prepared by Ti-biphenolate catalysts the average particle size was between 100 and 200 nm of 'as-synthesized' polymer.

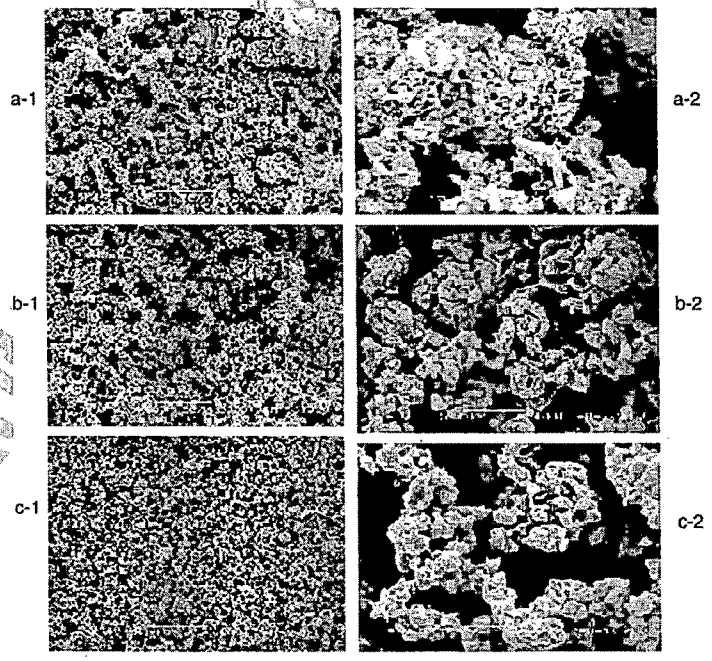
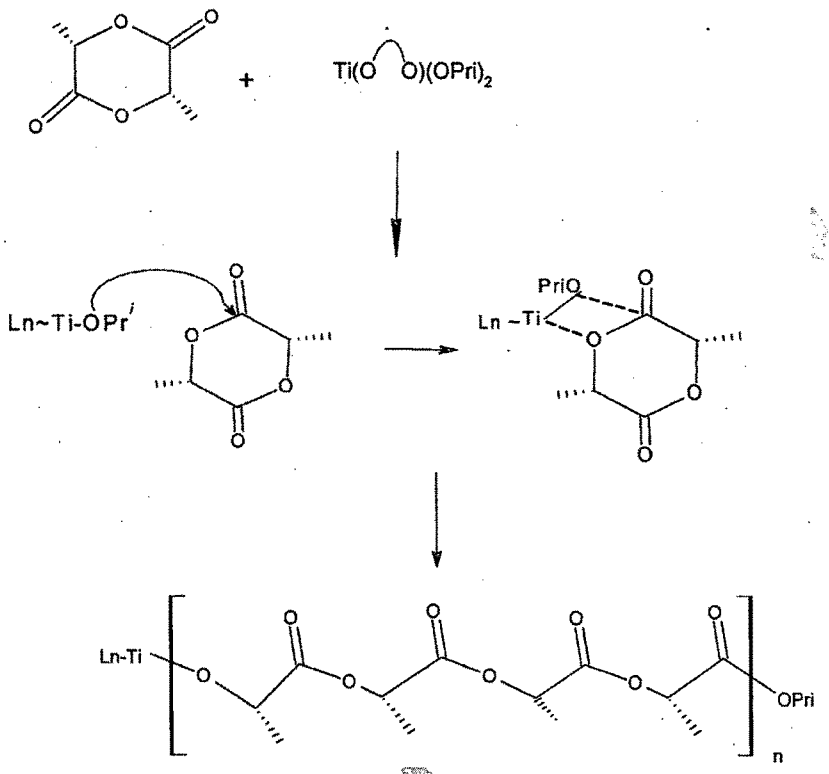



Fig. 9. SEM of L-PLA: Table 1, (a-1) entry 12 (500×), (a-2) entry 12 (5000×), (b-1) entry 7 (500×), (b-2) entry 7 (5000×), (c-1) entry 1 (500×) and (c-2) entry 1 (5000×).




Scheme 2. Proposed mechanism for ROP.

### 3.5. Mechanistic consideration

The NMR spectral profiles of PLAs lead us to speculate on the possible mechanistic pathway responsible for the polymerization of L-lactide. Initiation and propagation of isopropoxide catalyzed ROP was clearly evident but the termination may occur either by end capped Ti-biphenolate rests or by formation of cyclic oligomers [3,28]. Some of the key steps involved are outlined below (Scheme 2), which assumes an insertion–coordination pathway process as in the case of many other Lewis acidic metal alkoxide based initiators [29].

## 4. Conclusion

Well-defined biphenoxy-titanium alkoxide complexes were synthesized following a standard alcohol exchange protocol. All these metal complexes were found to be active in the melt polymerization of cyclic ester such as L-lactide while the catalytic activity was found to be strongly dependent on the reaction temperature and also on the duration of polymerization. Preliminary experiments show that higher reaction temperature favour the formation of high molar mass polymers and also improves the monomer conversion. The substituent effects on the biphenolate ligand was less pronounced in terms of overall productivity but the nature of Lewis acidic centre appears to contribute towards formation of highly crystalline polylactide albeit with very low molecular weights. Absence of intermolecular transesterifi tion during polymerization and the possibility of synthesiz PLAs having particle size close to the nano-region using no titanium based initiators holds promise for specific end appli tions.

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# Synthesis of ultra-low-molecular-weight polyethylene wax using a bulky Ti (IV) aryloxide–alkyl aluminum catalytic system

**Prashant S. Umare[1], Ajaykumar J. Tiwari[2], Robin Antony[2], Gopal L. Tembe[2]* and Bhavna Trivedi[1]**

[1]Department of Chemistry, The M.S. University of Baroda, Vadodara 390 002, India
[2]Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India

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TS1

**Complexes of titanium (IV) with bulky phenolic ligands such as 2-*tert*-butyl-4 methylphenol, 2, 4-di-*tert*-butyl phenol and 3,5-di-*tert*-butyl phenol were prepared and characterized. These catalyst precursors, formulated as $[Ti(OPh^*)_n(OPr^i)_{4-n}]$ ($OPh^*$ = substituted phenol), were found to be active in polymerization of ethylene at higher temperatures in combination with ethylaluminum sesquichloride ($Et_3Al_2Cl_3$) as co-catalyst. It was observed that the reaction temperature and ethylene pressure had a pronounced effect on polymerization and the molecular weight of polyethylene obtained. In addition, this catalytic system predominantly produced linear, crystalline ultra-low-molecular-weight polyethylenes narrow dispersities. The polyethylene waxes obtained with this catalytic system exhibit unique properties that have potential applications in surface coating and adhesive formulations. Copyright © 2007 John Wiley & Sons, Ltd.**

KEYWORDS: titanium–phenolate catalysts; ethylene polymerization; polyethylene wax; ethylaluminum sesquichloride

## INTRODUCTION

There has been an immense interest in the use of non-cyclopentadienyl catalysts for olefin polymerization over the past few years.[1–4] The replacement of ubiquitous 'Cp' ligand with hard donor ligands such as amido,[5,6] alkoxide,[7] siloxide[8] and aryl oxide[9–11] groups has tremendously expanded the scope of organometallic chemistry at early d-block metal centers.[12,13] One particular area of focus has been the application of titanium alkyloxides and aryloxides as precatalysts for novel types of $\alpha$-olefin polymerizations.[14–17] These titanium-based catalysts have also found extensive use in organic transformations such as oxidation,[18] epoxidation[19] and carbon–carbon bond formation.[20] Further, the diversity of these titanium complexes stems from the fact that $Ti(OR)_4$-type compounds are easily accessible and possess the ability to stabilize unusual coordination polyhedra, which have lead to the synthesis of two- and three-dimensional metal–organic frameworks.[21–23]

*Correspondence to: Gopal L. Tembe, Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India.
E-mail: gopal.tembe@ipcl.co.in

Industrial manufacture of polyethylene is primarily concerned with conventional grades such as low-density, high-density and linear-low-density polyethylenes (LDPE, HDPE and LLDPE). Nevertheless, new types of polyethylene as building blocks in chemical industry catalyst systems that are more active and selective are constantly being sought to meet the demand for polymer properties and minimize the cost of production. A potentially emerging segment of the global polyethylene business involves the production of specialty low-molecular-weight polyethylene wax, which is gaining importance for many applications.[24–27] Polyethylene wax (PE wax) can be made by direct polymerization of ethylene under controlled conditions. Another route involves breaking down high-molecular-weight polyethylene into lower-molecular-weight fractions. A third method involves separation of the low-molecular-weight PE fraction from high-molecular-weight polymer.

Commercial PE waxes, because of their unique physicochemical properties, serve as aids in a variety of plastics processing applications to enhance lubricity, control the set/softening point of hot melt adhesives, impart slip and rub resistance in printing inks and improve the fusing properties

in toner formulations, etc.[28–30] Wax producers like Clariant (Licowax), Dow (Insite catalyst) and Mitsui (Excerex process) employ proprietary metallocenes and methyl alumoxane as co-catalysts for polymerizing ethylene to highly crystalline low-molecular-weight polyethylene.[31–34] Synthetic PE waxes are generally characterized by low melt temperatures, high crystallinity, molecular weights from 1000 to 3000 g/mol and mean particle size around 10–30 μm. Compared with the relatively expensive metallocene technology, the design and development of non-metallocene homogeneous catalysts that are easily accessible, less expensive and tolerant to moisture and air for producing specialty PE wax, constitutes an useful research objective. However, there has been no systematic effort to study catalysts containing aryl oxides of group 4 metals, in particular those derived from sterically hindered phenols in ethylene polymerization. The aryloxides of titanium and zirconium described by the formulation $[(OR)_nMX_{4-n}$, where R = substituted phenol, X = labile ligand and M = Ti(IV) or Zr(IV)] are relatively ineffective in presence of MAO as co-catalyst for producing low-molecular-weight polyethylene.[35–40] In a recent finding we reported that titanium complexes of 1,1′-bi-2-aryl oxide, such as BINOL (1,1′-binaphthalene-2,2′-diol), which is an important $c_2$ symmetric chiral auxiliary ligand, promoted the polymerization of ethylene to predominantly low-molecular-weight product having high crystallinity and narrow polydispersity.[41] In order to gain further insight into the interesting behavior of bulky aryloxy derivatives of Ti(IV) in polymerization, in the present work, catalyst precursors containing sterically bulky phenols have been prepared and evaluated for catalytic ethylene polymerization in combination with ethyl aluminum sesquichloride as co-catalyst.

## RESULTS AND DISCUSSION

### Synthesis of aryloxide complexes of titanium

The preparation of Ti–phenolate complexes was carried out via the stoichiometric reaction between $Ti(OPr^i)_4$ and phenolic ligands [1 : 2 mole ratio in the case of **1** and 1 : 4 mole ratio in the case of **2–4**] and removal of liberated isopropanol azeotropically. The reaction in toluene afforded dark orange colored complexes.

### Catalyst characterization

The titanium complexes **1–4** described by the empirical formula $Ti(OPh^*)_n(OPr^i)_{4-n}$ are generally soluble in aromatic and chlorinated aromatic solvents but only sparingly so in aliphatic hydrocarbons. Catalysts **1–4** have been characterized by microanalysis, IR, $^1$H NMR, FAB mass spectra and thermal analysis. In a typical IR spectra of **1**, the low intensity broad peaks in the 3000–3500 cm$^{-1}$ region indicate deprotonation of the phenolate ligand on complexation to the titanium center.

The $^1$H NMR spectra are generally simple and were primarily used as a diagnostic tool for ascertaining the purity of the complexes (Fig. 1). A set of multiplets in the region 7.0–7.3 ppm for the aromatic protons is a common feature in addition to signals due to methyl proton at 2.36 ppm and tertiary butyl group {–C(CH$_3$)$_3$} at 1.3 ppm. In the FAB mass spectra of **3** a prominent peak for ligand fragment (phenol ion) appeared at 206. However, the parent ion was not detected. Fragment ions originating from other species were difficult to establish due to the complexity of the spectra beyond $m/z$ values of 400. Such band patterns were also noted in the EI-MS of other titanium alkoxide complexes.[4]

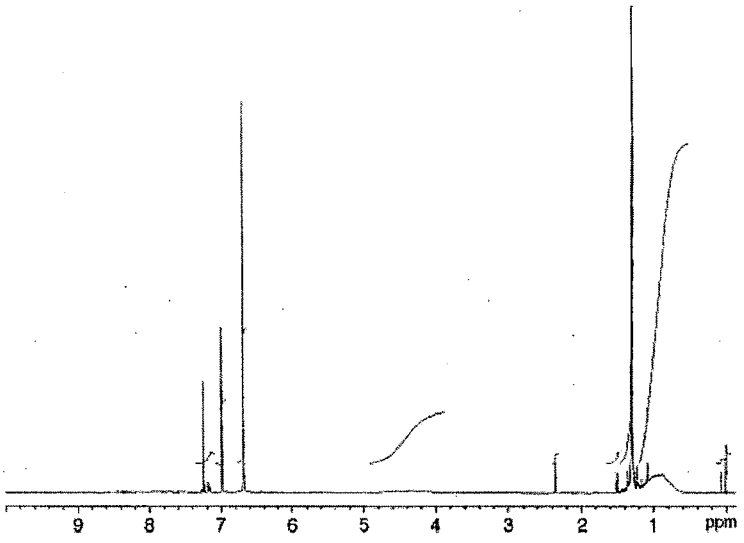


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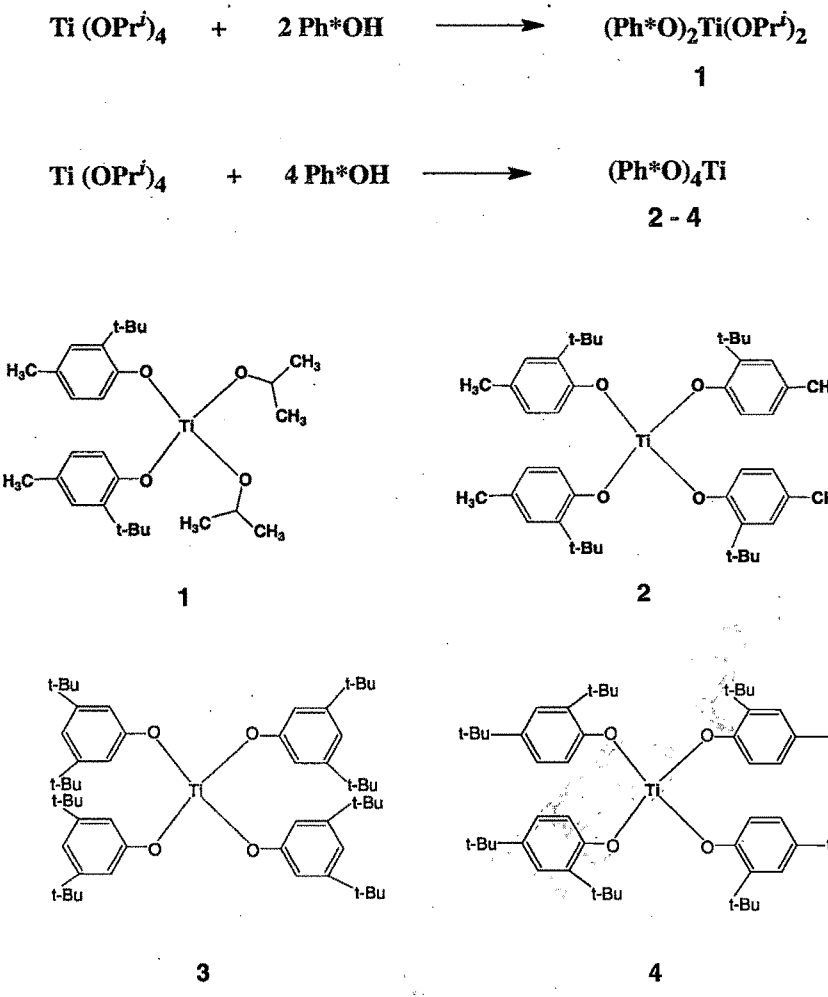
**Figure 1.** •$^1$H NMR of catalyst **3**.




**Scheme 1.** Catalyst synthesis. Ph*OH = 2-*tert*-butyl-4 methyl phenol (**1** and **2**); 3,5-di-*tert*-butyl phenol (**3**); 2,4-di-*tert*-butyl phenol (**4**).

In general the Ti catalysts are quite stable, as is apparent from the thermal degradation profile (Fig. 2), which indicates major degradation peaks in the 200–400 °C region. However, complete degradation to the dioxide, $TiO_2$, was noted beyond 480 °C. Typical TG results for **1** (observed 16.8%; calculated 16.2%) and **3** (observed 8.9%; calculated 9.2%) support the solid-state stoichiometry of the complexes inferred from microanalysis.

## Polymerization of ethylene

The results of ethylene polymerization using catalyst precursors **1–4** are shown in Table 1. The efficiency of catalysts was compared with known metallocenes such as $Cp_2TiCl_2$ and $Cp_2ZrCl_2$ in the presence of EASC as co-catalyst. The polymerization was carried out under different reaction conditions such as temperature, pressure, solvent and co-catalysts. Initial examination of catalysts indicated that, amongst the different substituted phenols, titanium complexes of 2-*tert*-buyl-4 methylphenol and 3, 5 di-*tert*-butyl phenol generally display higher activity in polymerization than the titanium complex of 2, 4 di-*tert*-butyl phenol (Table 1, entries 1–4). The metallocenes on the other hand are practically inactive under these reaction conditions (Table 1, entries 5 and 6). The activity is also predominantly dependent on the nature of the co-catalyst. Ethylaluminum sesquichloride uniquely favors the polymerization. Other chlorinated alkylaluminums, $EtAlCl_2$ (EADC; Table 1, entry 11), are also active but show lower productivities. This rather exclusive combination of Ti–phenolate precursor and EASC co-catalyst in polymerization suggests formation of active



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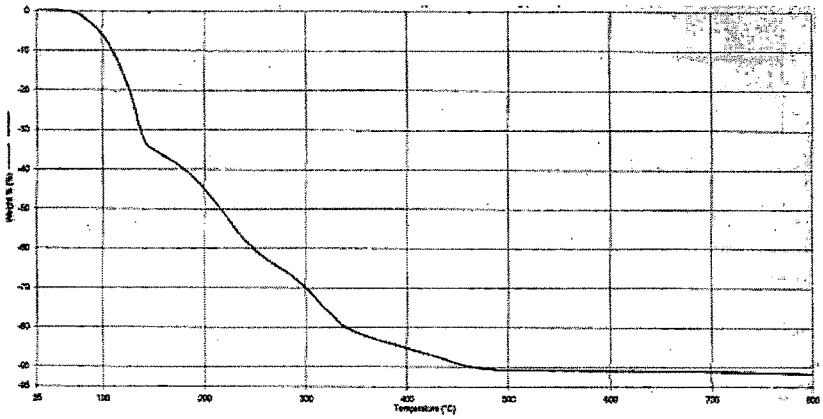

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**Figure 2.** Typical TG of catalyst **3**.

**Table 1.** Results of ethylene polymerization with Ti–phenolate catalytic system[a]

| Entry | Catalyst | Temperature, °C | Pressure, psi | Co-catalyst | Activity, kg PE/g Ti | $M_w$ | PD | $T_m$ (°C) | $d$ (g cm |
|---|---|---|---|---|---|---|---|---|---|
| 1 | **1** | 100 | 500 | EASC | 19.9 | 1290 | 1.5 | 118 | 0.95 |
| 2 | **2** | 100 | 500 | EASC | 24.7 | 1170 | 1.5 | 124 | 0.95 |
| 3 | **3** | 100 | 500 | EASC | 18.5 | 930 | 1.4 | 128 | 0.95 |
| 4 | **4** | 100 | 500 | EASC | 4.7 | 840 | 1.4 | 125 | 0.95 |
| 5 | $Cp_2TiCl_2$ | 100 | 500 | EASC | 0.2 | — | — | — | — |
| 6 | $Cp_2ZrCl_2$ | 100 | 500 | EASC | 1.0 | — | — | — | — |
| 7[b] | 2 | 100 | 250 | EASC | 9.5 | | | 116 | |
| 8[c] | 3 | 50 | 500 | EASC | 2.6 | | | — | |
| 9[d] | 3 | 30 | 500 | EASC | 0.3 | | | — | |
| 10 | 3 | 100 | 500 | MAO | 1.5 | | | 132 | |
| 11 | 3 | 100 | 500 | EADC | 4.2 | | | 123 | |
| 12 | 3 | 100 | 500 | TEAL | 0.2 | | | — | |
| 13[e] | 3 | 100 | 500 | EASC | 23.5 | | | 116 | |
| 14[f] | 3 | 100 | 500 | EASC | 0.1 | | | — | |

[a] All reactions were carried out in a 600 ml SS reactor at 100 °C and 500 psi ethylene pressure for 1h in toluene.
[b] ($C_2H_4$) = 250 psi; temperature = 50 °C[c], 30 °C[d]; [e] solvent = chlorobenzene;
[f] hexane.
EADC = $EtAlCl_2$, TEAL = $Et_3Al$.

intermediates responsible for polymerization, as will be discussed in the following section. Interestingly conventional co-catalysts for polyolefin production such as methyl alumoxane (MAO) and triethylaluminum (TEAL, $Et_3Al$; entries 10 and 12) displayed poor activity while the isolated polymer was found to be largely coarse and inhomogeneous. A noteworthy feature of polyethylene obtained with these Ti–phenolate catalysts is the invariably low molecular weight ($M_w$) of the polymer, as revealed by GPC analyses. In all cases the PEs display narrow molecular weight distribution ($M_w/M_n$ = 1.4–1.5). It is however, pertinent to point out that the tetra aryloxides of unsubstituted phenol 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 exclusive formation of solid PE wax with $(OPh^*)_n$ $(OPr^i)_{4-n}$]-type complexes employed in the pres study.[46,47] This can be qualitatively interpreted as the cl propagation rates, $r_p \approx r_t$ in the case of the $Ti(OR)_4$–E/ catalyst system, resulting in oligomer formation whe with the $[Ti(OPh^*)_n(OP^i)_{4-n}]$–EASC system $r_p > r_t$, giv polyethylene under identical conditions. The absence $\alpha$-olefins was also confirmed by gas chromatograp analysis of reaction mixture after separation of polyr Detailed studies on the effect of temperature (entries and 9) and pressure (entries 3 and 7) were then car out employing complex **3** and EASC as the co-catal From the results summarized in Tables 1 it is evi that increasing the reaction temperature from ambien



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100 °C has a marked effect on the activity as seen by the approximately 10-fold increase in polymer yield. Applying higher pressure while maintaining constant temperature led to higher productivity. Generally a combination of higher Al:Ti ratio and higher temperature led to an improvement in the productivity of the catalyst. A brief study of the effect of different solvents (Table 1, entries 13 and 14) indicated that a chlorinated aromatic solvent such as chlorobenzene showed a nearly 25% increase in productivity of polyethylene over toluene. Interestingly, this increase was accompanied by a slight increase in $M_w$. However, aliphatic hydrocarbon solvents such as hexane resulted in poor activity, which may be due to low solubility of catalysts in these solvents.

In order to ascertain the level of branching in the 'as synthesized' polymer reported in Table 1, the IR spectrum was compared with a standard PE wax sample using the following equation.[48] The branching degree of PEs was determined by taking the value of absorbance of the 1378 $cm^{-1}$ peak (νs $CH_3$)

$$\frac{n}{1000C} = \frac{(A_{1378}/l\rho)\ 5.4}{0.691}$$

From the spectrum shown in Fig. 2 the reference material indicated a branching degree of **4** compared with **1.9** for the sample. These values are consistent with generally fewer short chain branches (SCB) observed for most linear high density polyethylenes (~1–2/1000C).

To investigate the molecular properties of polyethylenes further, they were characterized by GPC (Fig. 3). A commercial PE wax sample was also included as a reference for comparison. The GPC of this material also displays similar distribution in the low-molecular-weight region. As discussed earlier, one of the striking feature of these PEs is the exceptionally low molecular weights ($M_w$ = 840–1290) and narrow polydispersities (PD = 1.4–1.5). In no case was high-molecular-weight PE ($M_w \geq \sim 10^5$) obtained, although these catalysts resemble typical Ziegler–Natta systems. As briefly mentioned in the Introduction, polyethylene waxes with interesting applications have similar molecular weights and molecular weight distributions. The DSC (Fig. 4) also reveals lower $T_m$ than that observed for conventional HDPE or LDPE. A known sample of micronized PE wax was used as benchmark for comparison of polymer properties with that obtained in this work (The commercial samples employed in this work, MPP123 and MPP 635 are a micronized, high-melting-point, crystalline form of polyethylenes and were supplied by M/s Micro Powders Inc., USA. The products have a $T_m$ of 125-135 °C, molecular weight 2000, $d$ (25 °C) 0.96 and maximum particle size = 31 μm. These and other grades of polyethylene waxes have been designed to increase the abrasion resistance and anti-blocking characteristics in flexographic inks as well as industrial paints and coatings. More details can be found at www.micropowders.com).

The intensity of the equatorial peaks in the X-ray diffractogram (Fig. 5) for the 110 ($2\theta = 21.5°$) and 200 ($2\theta = 23.5°$) 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.

The crystalline nature of these polymers was also estimated by integration of the X-ray diffraction peaks observed for the

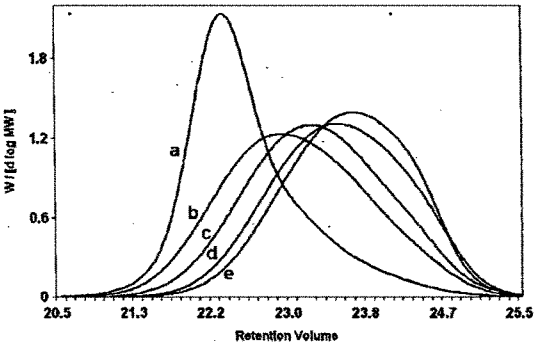


**Figure 3.** •GPC profile of polymer listed in Table 1: (a) commercial sample; (b) Table 1, entry 3; (c) Table 1, entry 2; (d) Table 1, entry 4; (e) Table 1, entry 1.

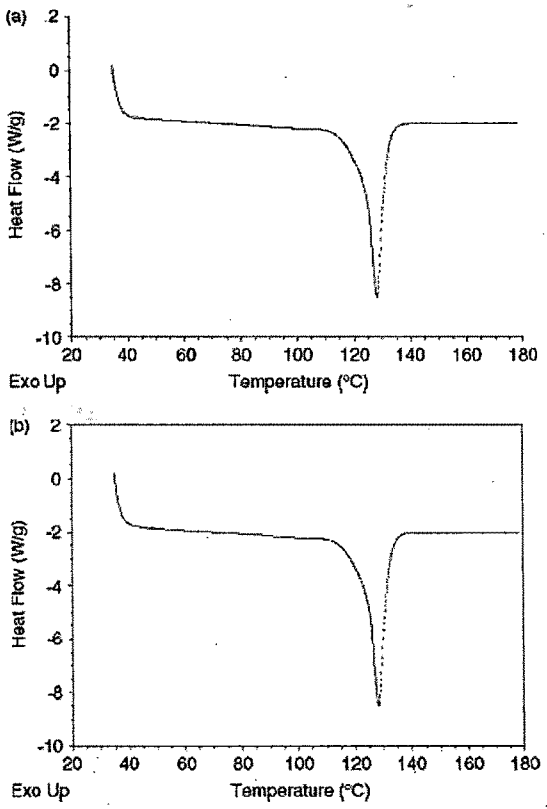


**Figure 4.** •DSC of PE wax, Table 1: (a) entry 2; (b) entry 3.




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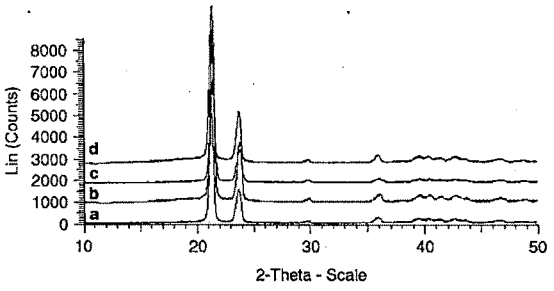


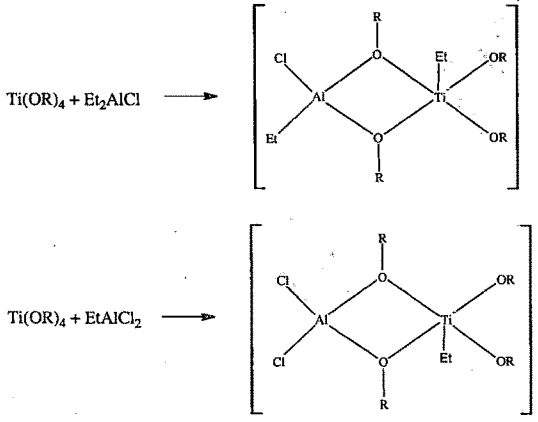

AQ6

**Figure 5.** •XRD of PE wax (a) commercial sample; (b) Table 1, entry 1; (c) Table 1, entry 2; (d) Table 1, entry 3.

wax samples. A high degree of crystallinity is indicated in all cases, generally in the range 80–88%. The polymer particles appear as well separated crystalline blocks having sharp plate-like features, as seen by a scanning electron micrograph. A common feature of these waxes is that the average particle size of the polymer as measured during post-reactor work-up was typically <400 μm. In Fig. 6 is shown the SEM of one of the PE samples obtained in this study. The unique polymer properties exemplified by these titanium phenolate–EASC catalyst system can be fine-tuned to tailor the $M_w$ and polydispersities for the end use application.

## Catalytic pathway

Treatment of mononuclear $Ti(OR)_4$-type alkoxides with alkylaluminum halides has been reported to yield active intermediates (see below) responsible for the polymerization of ethylene to low-molecular-weight dimers and oligomers, which essentially follow Schulz–Flory-type distribution.[49–53]




We believe that a similar type of active species may be involved in the present Ti–phenolate system. Moreover, as EASC is derived from an equimolar mixture of EADC and DEAC,[54] we have

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

Since EASC can dissociate as $Et_2AlCl$ and $EtAlCl_2$ in solution, it is reasonable to expect the formation of two types of catalytic species on interaction with Ti–phenolate catalyst. The reduction of Ti(IV) in the presence of EASC will generate catalytically active Ti-alkyl intermediates.

Qualitative information on the course of reaction was followed with the help of UV–vis spectra at different stages of mixing of the catalyst precursor and EASC in toluene. For example, in Fig. 7 the peak at 365 nm after immediate addition of EASC to catalyst **1** disappears (intensity is reduced). The introduction of ethylene leads to a new peak at around 460 nm (LMCT band). Similar evidence for the formation of active Ti-alkyl species was proposed for ethylene polymerization using a metallocene $Cp_2TiCl_2$ and MAO by Kaminsky and others.[55,56]

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.[57]

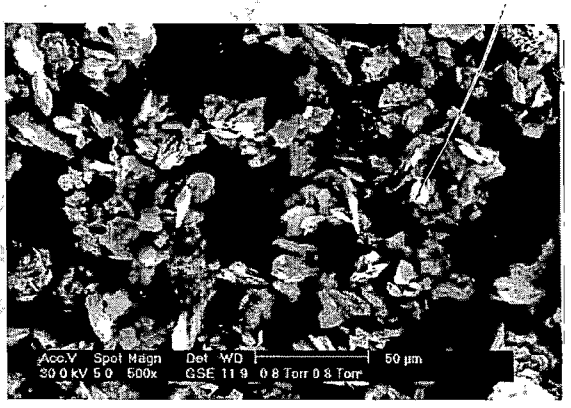
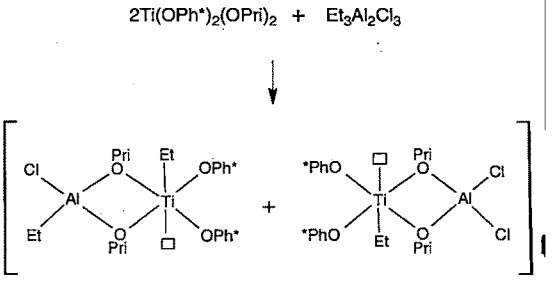
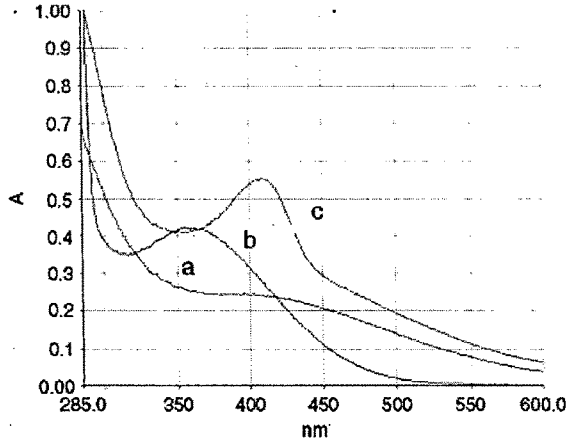



**Figure 6.** SEM of PE wax (Table 1, entry 1).

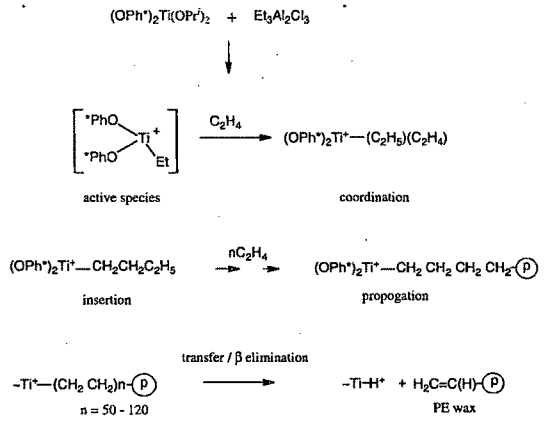



**Scheme 2.** Reaction of catalyst **1** with EASC.




AQ7

**Figure 7.** •UV spectrum, (a) catalyst **1** + EASC; (b) catalyst **1**; (c) catalyst **1** + EASC + $C_2H_4$.




**Scheme 3.** Proposed mechanism of ethylene polymerization by Ti–phenolates.

In the present Ti–phenolate catalytic system, higher temperatures tend to favor formation of active intermediates responsible for polymerization.

## Mechanistic aspect

From the information collected in Table 1 it follows that for the different Ti–catalyst precursors examined in this study, the activities and molecular weight dependence are primarily governed by (1) the nature of the substituents; (2) the type of alkyl aluminum co-catalyst; and finally (3) the reaction conditions of polymerization.

Based on a theoretical study by Morokuma[58,59] on the catalytic polymerization by chelating bridged and non-bridged Titanium aryloxides, it is possible to predict the possible course of ethylene polymerization for the present Ti–phenolate–EASC catalytic system. The active cationic species generated from the *'pre* catalyst' intermediates shown in Scheme 2 will facilitate the insertion of ethylene (rate determining step) into the growing chain, which ultimately leads to the desired polyethylene via propagation and termination steps. A modified Cossee–Arlmann-type mechanism[60–62] can thus be extended to rationalize the polyethylene formation with these catalysts (Scheme 3).

Although chain transfer can occur by other reactions as well, however, the relative inactivity of these catalysts with MAO & $Et_3Al$ indicates that termination is unlikely to proceed by transfer to Al-alkyl or by $H_2$ under the reaction conditions. It is obvious that steric factors in phenols and the coordination geometry around the Ti atom contribute significantly towards productivity and *inter alia* molecular weight regulation.[63,64] This implies that the ligands that generate the highest molecular weights do so by slowing down $\beta$-hydrogen abstraction. Although the structure of active intermediates is as yet unknown, the mechanism leading to these linear low-molecular-weight polyethylenes is consistent with those reported previously for solution phase olefin polymerization using titanium alkoxides and aluminum alkyls.[58,59,65,66] Efforts are underway to investigate the detailed kinetics of this reaction.

## CONCLUSIONS

The complexes of titanium (IV) with bulky phenolic ligands in presence of ethylaluminum sesquichloride as co-catalyst are highly effective for the synthesis of specialty low-molecular-weight polyethylene with good productivity. The catalyst activity is significantly influenced by the reaction temperature and Al:Ti ratios. The physical properties exhibited by these polyethylenes such as low molecular weights, high crystallinity and narrow dispersities suggest single-site catalytic behavior of Ti-aryloxy precursors. The close resemblance of polymer properties to commercially important synthetic waxes holds promise for developing alternative cheaper catalysts for this process.

## EXPERIMENTAL

### Materials

The synthetic work involving air- and/or moisture-sensitive compounds was carried out using standard high vacuum Schlenk or dry box (VAC) technique. AR-grade toluene was refluxed over sodium for 4 h and freshly distilled prior to use. High-purity ethylene (polymer grade) was collected in a cylinder from the commercial plant, the pressure of which was adjusted with a two-stage regulator. Co-catalysts were purchased from Ethyl Corporation or Crompton GmbH and used without further purification. Titanium iso-propoxide and the different substituted phenols were purchased from Aldrich and used as received.

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## Elemental analysis

Elemental analyses was carried out on a Perkin Elmer Model 2400 instrument. Titanium content in catalysts was determined gravimetrically as $TiO_2$.

## IR spectra

A Perkin Elmer FT-IR spectrometer model Spectrum BX was used to obtain the IR spectra of samples pressed into KBr pellets over the 4000–400 $cm^{-1}$ range.

## NMR analysis

$^1H$ 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 spectra

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 were recorded at room temperature. *m*-Nitrobenzyl alcohol was used as the matrix.

## UV–vis spectra

UV–vis spectra of Ti–catalyst and EASC were separately taken in toluene solutions and sealed in 1 cm airtight quartz cells under nitrogen atmosphere. The spectra were then recorded on a Perkin-Elmer Lambda 19 UV–vis–NIR spectrophotometer in the 200–800 nm range at ambient temperature; $2.0 \times 10^{-4}$ mmol solution of the catalyst in toluene was taken for recording the spectra.

## Gel permeation chromatography

Molecular weights of polyethylene were determined using size exclusion chromatography (SEC). The high-temperature GPC analysis of the polymers was carried out using Polymer Lab's PL-GPC 220 chromatograph. A set of PL Gel three Mixed B columns were used. 1,2,4-Trichlorobenzene was used as the mobile phase at 135 °C. Irganox, 0.0125%, was added to the mobile phase prior to filtration. A sample preparation unit, PL-SP260, was used to dissolve and filter the samples at 135 °C; 0.2% solutions were injected with the help of an auto sampler to record the chromatogram. Viscotek's Trisec conventional software was used to analyze the chromatograms which were matched with polystyrene calibration curve. The following MHK constants were used to construct an universal calibration curve. For PS: $K = 1.2105 \times 10^{-4}$; $a = 707$; PE: $K = 4.055 \times 10^{-4}$; $a = 725$.

## Differential scanning calorimetry

Differential scanning calorimetry was performed under 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.

## Thermogravimetry

TGA/DTA of catalysts were recorded in air (heating rate 10 °C/min) from ambient to 800 °C on a TA Instrument (Universal V2).

## Density of polymer

The density of polymers was determined in *n*-butyl acetate medium at 23 °C as per ASTM method D 792-00.

## X-ray diffraction

X-ray experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled CuK$\alpha$ radiation ($\lambda = 1.5406$ 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 $2\theta$ ranges from 10–50° at a rate of 1 deg/min. Measurements were recorded at steps of 0.02°.

## Scanning electron microscopy

Scanning electron micrographs of powdered polymer samples were taken on a Jeol JFC 1100 instrument ion sputter water. They were observed on a Jeol 5600 CV scanning electron microscope in Hv mode with operating voltage of 20 kV.

## Catalyst 1 preparation

To a solution of 1 mmol (284.3 mg) of $Ti(OPr^i)_4$ in toluene (25 ml) was added slowly 2 mmol (324.5 mg) of 2-*tert*-butyl-4 methyl phenol 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, the precipitated solid washed with small portions of toluene and finally the dark orange-colored complex was isolated. The remaining catalysts **2–4** were prepared in an analogous manner by using the corresponding amount of substituted phenol as the case may be. Anal calcd for catalyst **1** ($C_{28}H_{44}O_4Ti$), C, 68.3; H, 9.0; Ti, 9.7; found: C,68.2; H 8.8; Ti, 9.8. Catalyst **2** ($C_{44}H_{60}O_4Ti$), C, 75.4; H, 8.6; Ti, 6.8; found: C,75.8; H 8.6; Ti, 6.9. Catalyst **3** ($C_{56}H_{84}O_4Ti$), C, 77.4; H, 9.7; Ti, 5.5; found: C,77.8; H 10.1; Ti, 5.5. Catalyst **4** ($C_{56}H_{84}O_4Ti$), C, 77.4; H, 9.7; Ti, 5.5; Found: C,77.5; H 9.8; Ti, 5.8.

## Procedure for ethylene polymerization

Ethylene polymerization was conducted in an high-pressure stirred autoclave (600 ml, Parr, USA) connected to a model 4850 microprocessor controller. Prior to polymerization, the reactor was baked at 150 °C under nitrogen for 2 h and then cooled to room temperature. In a typical experiment catalyst **1** (13.8 mg, 0.028 mmol) dissolved in toluene (50 ml) and $Et_3Al_2Cl_3$ (1.28 ml, 5.6 mmol) in toluene (200 ml) were carefully charged into the reactor under a nitrogen blanket. The Al : Ti molar ratio was 200. The reactor temperature was set at 100 °C and then pressurized with ethylene to 500 psi. The polymerization was continued for 1 h. After the end of the




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reaction the autoclave was cooled to ambient, excess ethylene vented 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 70 °C for 2 h.

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