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Prashant S. Umare^a; Karumanchi Rao^b; Gopal L. Tembe^b; Deepa A. Dhoble^c; Bhavna Trivedi^a

^a Department of Chemistry, The M.S. University of Baroda, Vadodara, India ^b Research Centre, Indian Petrochemicals Corporation Limited, Vadodara, India ^c Division of Polymer Science and Engineering, National Chemical Laboratory, Pune, India

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Polyethylene Waxes: Catalytic Synthesis by Ti-Biphenolates

PRASHANT S. UMARE,¹ KARUMANCHI RAO,² GOPAL L. TEMBE,² DEEPA A. DHOBLE,³ and BHAVNA TRIVEDI¹

¹Department of Chemistry, The M.S. University of Baroda, Vadodara, India

²Research Centre, Indian Petrochemicals Corporation Limited, Vadodara, India

³Division of Polymer Science and Engineering, National Chemical Laboratory, Pune, India

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Soluble complexes of Ti (IV) bearing biphenol groups such as 1,1'-binaphthelene 2, 2' diol (Binol), 1,1'-methylene di-2-naphthol, biphenol were prepared and characterized. These catalyst precursors formulated as [Ti(O-O)(OPr^t)Cl] are found to be active in polymerization of ethylene at high temperatures in combination with ethylaluminum sesquichloride (Et₃Al₂Cl₃) as co-catalyst. The ultra low-molecular weight polyethylenes are linear, crystalline and display narrow polydispersities. The PE waxes obtained with this catalytic system exhibit unique properties that have potential applications in surface coating and adhesive formulations.

Keywords: titanium-biphenolate catalysts; ethylene polymerization; polyethylene wax; ethyl aluminum sesquichloride

1 Introduction

Due to the industrial importance of new types of polyethylenes as building blocks in chemical industry catalyst systems that are more active and selective are constantly being sought to match the demands of polymer properties and minimize the cost of production. In the case of ethylene, apart from the conventional grades such as low density, high density and linear low density polyethylenes (LDPE, HDPE and LLDPE) a potentially emerging segment of global polyethylene business involves the production of specialty low molecular weight polyethylene wax which is gaining importance for many applications (1–3). 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 physico-chemical properties, serve as aids in a variety of plastics processing applications to enhance lubricity, controlling set/softening point of hot melt adhesives, impart slip and rub

resistance in printing inks and improve the fusing property in toner formulations etc. (4, 5).

In contrast to commodity polyethylenes synthetic PE waxes are generally characterized by lower melt temperatures, high crystallinity, molecular weights from 1000–3000 gm/mole and mean particle size around 10–30 microns for end use. Thus, a major strategy for precise control of molecular weights and M_w/M_n of polyethylene involves the design of suitable catalysts and olefin polymerization under controlled conditions. Wax producers like Clariant (Licowax), Dow (Insite catalyst) and Mitsui (Excercex process) employ proprietary metallocenes and methyl alumoxane as co-catalyst for polymerizing ethylene to highly crystalline low molecular weight polyethylene (6–8). Compared to 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.

A review of recent literature indicates an increase in the application of new families of non-Cp based catalyst precursors for ethylene polymerization. These have mainly led to high molecular weight polyethylene or in some instances linear alpha olefins with moderate to good selectivity (9, 10). The most notable catalysts in this category employ tridentate (N-N-N) and bidentate (O-N) Schiff base complexes of late transition metals (11, 12).

However, there has been no systematic effort to study catalysts containing aryl oxides of group 4 metals, in particular,

Address correspondence to: G. L. Tembe, Research Centre, Indian Petrochemicals Corporation Limited, Vadodara 391 346, India. Tel.: +91-0265-6696492; Fax: +91-0265-6693934; E-mail: gopal.tembe@ipcl.co.in

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).

The aryl oxides 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 the presence of MAO as co-catalyst for producing low molecular weight polyethylene (1, 18–22). In a previous work, we showed that under optimum conditions it is possible to oligomerize ethylene to linear α -olefins using Ti(IV) aryloxo complexes of monodentate phenols of the type $M(OR)_4$ in the presence of alkylaluminum halide co-catalysts other than MAO (23). 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 a predominantly low molecular weight product having high crystallinity and narrow polydispersity (24). In order to gain further insight into the interesting behavior of aryloxo derivatives of Ti(IV) in polymerization, in the present work, a broad group of catalyst precursors containing unsubstituted bi and mono phenols have been prepared and evaluated for catalytic ethylene polymerization in combination with ethyl aluminum sesquichloride as co-catalyst. The nature of ancillary ligands around Ti, as well as the effect of steric bulk of biphenols on overall productivity to PE wax with desired molecular characteristics has been described.

2 Experimental

2.1 Materials

The synthetic work involving air and/or moisture-sensitive compounds was carried out using a standard high vacuum Schlenk or dry box (VAC) technique. A.R 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 *tri* iso-propoxide chloride and the different bi/mono phenols were purchased from Aldrich and used as received.

2.2 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 to 400 cm^{-1} range. The $^1\text{H-NMR}$ spectrum of catalysts was recorded in CDCl_3 solvent on a Varian NMR 300 MHz spectrometer using TMS as an internal reference. FAB mass spectral analysis of catalysts was carried out on a JEOL

SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon as the FAB gas. The accelerated voltage was 10 kV and the spectra recorded at room temperature.

m-nitrobenzyl alcohol was used as the matrix. For the UV-Vis spectra Ti-catalyst precursor 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. 2.0×10^{-4} mmole solution of the catalyst in toluene was taken for recording the spectra.

Molecular weights of polymers 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 . 0.0125% Irganox 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: $K = 1.2105e^{-4}$; $a = 707$; PE: $K = 4.055e^{-4}$; $a = 725$. 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 $10^\circ\text{C}/\text{min}$. Indium was used to perform the calibration. TGA/DTA of catalysts were recorded in air (heating rate $10^\circ\text{C}/\text{min}$) from ambient to 600°C on a TA Instrument (Universal V2). Density of polymers was determined in *n*-butyl acetate medium at 23°C as per ASTM method D 792-00. X-ray experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled $\text{CuK}\alpha$ radiation ($\lambda = 1.5406\text{ \AA}$, generator voltage = 45 kV, current = $40\text{ }\mu\text{A}$) in the reflection mode, detected by a scintillation counter. Samples were pressed films approximately $400\text{ }\mu$ thick and were scanned into 2θ ranges from 15° – 45° at a rate $1^\circ/\text{min}$. 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.

2.3 Catalyst Preparation

Catalyst **1** was synthesized by a modified literature procedure (25). To a solution of 1 mmol (284.3 mg) of $\text{Ti}(\text{OPr}^i)_3\text{Cl}$ in toluene (25 mL) was added slowly 1 mmol (284.0 mg) of 1,1' binaphthalene-2,2'-diol (Binol) ligand in warm toluene (30 mL) under nitrogen atmosphere and heated at 60°C for 3 h. The contents were then stirred for 24 h at room temperature. The solvent was carefully removed, precipitated solid washed with small portions of toluene and finally the

orange colored complex was isolated. The remaining catalysts **2–4** were prepared in an analogous manner by using the corresponding bi/mono phenol as the case may be. Anal. calcd. for catalyst **1** ($C_{23}H_{19}O_3ClTi$); C, 64.7; H, 4.5; Ti, 11.22; Found: C, 64.2; H, 4.9; Ti, 11.9. 1H -NMR ($CDCl_3$, 300 MHz), 7.08–8.82 (12H, aromatic protons), 1.19 (6H, $CHMe_2$), 3.88 (1H, $CHMe_2$); catalyst **2** ($C_{24}H_{21}O_3ClTi$); C, 65.4; H, 4.8; Ti, 10.9; Found: C, 65.7; H 4.6; Ti, 11.1. 1H -NMR 7.02–8.76 (12H, aromatic protons), 1.21 (6H, $CHMe_2$), 3.49 (1H, $CHMe_2$), 4.74 (2H, CH_2 bridge); catalyst **3** ($C_{15}H_{15}O_3ClTi$); C, 55.2; H, 4.6; Ti, 14.7; Found: C, 55.3; H 4.9; Ti, 14.4. 1H -NMR 7.02–7.35 (8H, aromatic protons), 1.22 (6H, $CHMe_2$), 4.04 (2H, $CHMe_2$) and catalyst **4** ($C_{15}H_{17}O_3ClTi$); C, 54.8; H, 5.2; Ti, 14.6; Found: C, 54.7; H 5.0; Ti, 14.3. 1H -NMR 6.82–7.25 (10H, aromatic protons), 1.24 (6H, $CHMe_2$), 4.10 (2H, $CHMe_2$).

2.4 Ethylene Polymerization

Ethylene polymerization was conducted in a high-pressure stirred autoclave (600 mL, Parr, USA) connected to a model 4850 microprocessor controller. Prior to polymerization, the reactor was baked at $150^\circ C$ under nitrogen for 2 h and then cooled to room temperature. In a typical experiment catalyst **1** (12.0 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 $100^\circ C$ and then pressurized with ethylene to 300 psi. The polymerization was continued for one hour. After the end of the 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 $70^\circ C$ for 2 h.

3 Results and Discussion

3.1 Synthesis of Aryloxyde Complexes of Titanium

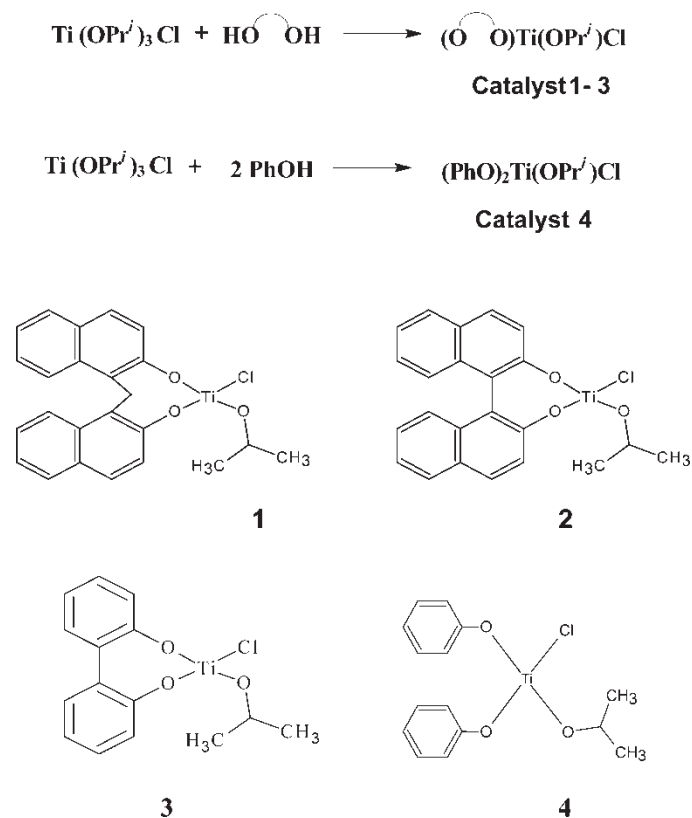
The preparation of Ti-biphenolate complexes could be realized via one of the following three synthetic routes (a) stoichiometric reaction between $Ti(OPr^i)_3Cl$ and the biphenol (alcohol exchange) and separation of liberated *iso*-propanol by azeotropic/vacuum distillation b) treatment of a lithium salt of biphenol ($LiOR$) with $Ti(OPr^i)_3Cl$ followed by removal of $LiCl$ and (c) low temperature reaction between phenolic ligands and $TiCl_4$ in presence of a base (usually tertiary amine) for eliminating the HCl formed. Method (a) was chosen in this work for isolating the Ti-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

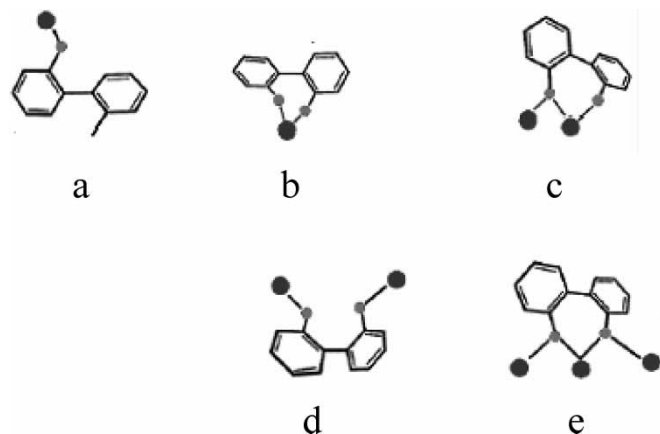
The stoichiometric reaction between $Ti(OPr^i)_3Cl$ and phenolic ligands [1:1 mole ratio in case of **1–3** (biphenol) and 1:2 mole ratio in **4** (mono phenol)] in toluene solution afforded dark orange coloured complexes. The Ti complexes described by the empirical formulation $Ti(Biphenol)(OPr^i)Cl/Ti(phenol)_2(OPr^i)Cl$ are generally soluble in aromatic and chlorinated aromatic solvents but only sparingly so in aliphatic hydrocarbons.

In the biphenol case, theoretically the ligand can bind to the titanium metal center in at least five different ways as shown in Scheme 2.

However, the most abundantly formed complexes are those with biphenol in the chelating mode (b) and to a lesser extent as in (c) (26). In the absence of other ligands, the Lewis acidity of the titanates is enhanced greatly so that coordinative unsaturation is overcome by the formation of aggregates. Depending on the molar ratio of the starting $Ti(OPr^i)_4$ precursor and biphenol a variety of complexes have been isolated previously by Heppert and Walsh but only a limited number of which have been characterized by X-ray crystal structure analysis (27, 28). Catalysts of the type **1** have been shown to exist as a dimer in the solid state based on X-ray analysis (29). Thus, for catalyst **1**, we can envisage that the monomeric $Ti(O-O)(OPr^i)Cl$ can undergo facile



Sch. 1. $o\text{-}o = \text{binol}$, [**1**]; 1,1'-methylene-2-naphthol, [**2**]; Biphenol, [**3**].

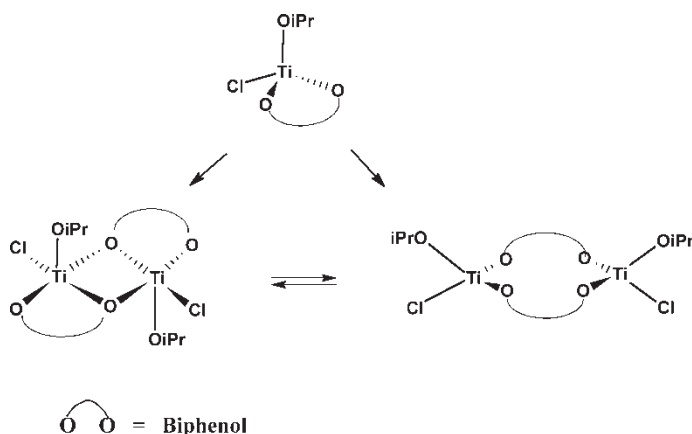


Sch. 2. Coordination modes of the 2,2'-biphenolate ligand: (a) monodentate mode, (b) chelate (O,O') mode, (c) bridging chelate (O,O,O') mode, (d) bridging μ_2 -(O,O') mode, (e) doubly bridging chelate μ_3 -(O,O,O',O') mode.

inter or intramolecular exchange in solution leading to dimeric forms as indicated by the following equilibria (Scheme 3) between the two types of species (30).

With increasing steric bulk of the biphenolate ligands, the tendency to form higher aggregates in the solid diminishes. Such a phenomena has previously been observed in other Ti-diolate catalysts (31). The catalysts **1–4** have been characterized by microanalysis, IR, $^1\text{H-NMR}$, FAB mass spectra and thermal analysis. In a typical IR spectra of **1** the low intensity broad peaks in the $3000\text{--}3500\text{ cm}^{-1}$ region indicate deprotonation of the biphenolate ligand. Other characteristic peaks of **1** and their assignments are (in cm^{-1}): 3487mbr ($\nu\text{O-H}$), 3056m ($\nu\text{bph C-H}$), 2960m ($\nu\text{as CH}_3$), 1595m , 1502s ($\nu\text{bph-Ti C-C}$), 1463s ($\delta\text{as CH}_3$), 1432s , 1263s , 1227s ($\nu\text{bph-Ti C-O}$), 1147w (Pr^i), 1100s ($\delta\text{bph-Ti C-H}$), 1006m ($\nu\text{PrO-Ti C-O}$).

The $^1\text{H-NMR}$ spectra are generally simple and was primarily used as a diagnostic tool for ascertaining the purity of complexes. A set of multiplets in the region $7.5\text{--}8.5\text{ ppm}$ for the aromatic protons was a common feature in addition signals due to methyl protons of *iso*



Sch. 3. Possible solid state equilibria in catalysts.

propyl group ($1\text{--}1.2\text{ ppm}$) were observed. In the FAB mass spectra a prominent peak for ligand fragment (biphenolate ion) appears at 186. However, the parent ion was not detected but the molecular ion peak at 233 was assigned to species which corresponds to parent ion minus coordinated alkoxide and chloride. Fragment ions originating from dimeric or trimeric species were difficult to establish due to complexity of the spectrum beyond m/z values of 400. Similar band pattern was noted in the EI-MS of other dimeric Titanium alkoxide complexes (27a, 32).

In general, the Ti catalysts are quite stable as is apparent from the thermal degradation profile (Figure 1) which indicates a degradation peak around 380°C assigned to the partial loss of biphenol ligand (obs. 39%; cal. 43%). However, complete degradation to the dioxide, TiO_2 was noted beyond 450°C (obs. 28%; cal. 25%) for this catalyst.

3.3 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 the known metallocene catalysts Cp_2TiCl_2 and Cp_2ZrCl_2 in presence of EASC as co-catalyst. The polymerization was carried out under different reaction conditions such as temperature, pressure, solvent and co-catalysts. Our initial examination of catalysts indicate that amongst the different biphenols, titanium complexes of 1,1'-binaphthalene 2,2'-diol and 1,1'-methylene di-2-naphthol generally display higher activity in polymerization. The metallocenes on the other hand are practically inactive under these reaction conditions (Table 1, entry 5, 6). The activity is also predominantly dependent on the nature of the co-catalyst. Ethylaluminum sesquichloride uniquely favours the polymerization. Other chlorinated alkyl aluminums Et_2AlCl (DEAC) and EtAlCl_2 (EADC) are also active but with showed lower 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

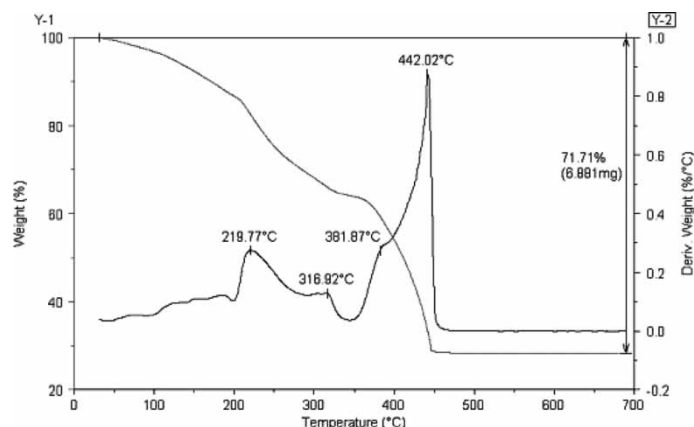


Fig. 1. TG/DTA of catalyst 3.

Table 1. Ethylene polymerization with Ti-biphenolate–EASC catalyst system

Entry	Catalyst	Activity Kg PE/g Ti	M _w	PD	T _m °C	d(g/cc)
1	1	9.5	1290	1.5	118	0.956
2	2	7.2	1170	1.5	119	0.954
3	3	5.2	930	1.4	110	0.955
4	4	4.2	840	1.4	105	0.958
5	Cp ₂ TiCl ₂	0.2	—	—	—	—
6	Cp ₂ ZrCl ₂	1.0	—	—	—	—

following section. Interestingly conventional co-catalysts for polyolefin production such as methyl alumoxane (MAO) and triethyl aluminum (TEAL, Et₃Al) display poor activity with the isolated polyethylene being largely coarse and inhomogeneous (Table 2). A noteworthy feature of polyethylene obtained with these Ti-biphenolate 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 = 1.4–1.5). It is however, pertinent to point out that the monosubstituted tetra aryloxides of titanium such as Ti(OR)₄ essentially leads to low molecular weight linear alpha olefins in the C₄–C₂₀ carbon range in sharp contrast to exclusive formation of solid polyethylene with Ti(O–O)(OPr^t)Cl type complexes employed in the present study (23). This can be qualitatively interpreted as the chain propagation rates, r_p ≅ r_t in the case of Ti(OR)₄–EASC catalyst system resulting in oligomer formation whereas with Ti(O–O)(OPr^t)Cl–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 the reaction. Detailed studies on the effect of temperature and pressure were then carried out employing complex **1** and EASC as the co-catalyst. From the results

summarized in Table 3, it is evident that increasing the reaction temperature from ambient to 100 °C has marked effect on the activity as seen by manifold increase in polymer yield. (Table 3, entry 1 and 3). The effect of ethylene pressure has been compiled in Table 4. Optimum pressure for good activity was around 300 psi at 100 °C and Al/Ti ratio of 200 (Table 4). Applying higher pressure under similar conditions leads to higher productivity. Generally, a combination of higher Al/Ti ratio and higher temperature lead to improvement in productivity of the catalyst. A brief examination of effect of different solvents (Table 5) indicated that chlorinated aromatic solvent such as chlorobenzene showed a ~30% increase in productivity of polyethylene than that for toluene. Interestingly, this increase is 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 spectra was compared with a standard PE wax sample by using the

Table 2. Effect of co-catalysts on ethylene polymerization at 100 °C^a

Entry	Co-catalyst ^b	Activity Kg PE/g Ti	T _m °C
1	EASC	9.5	118
2	DEAC	6.7	113
3	MAO	2.1	136
4	EAD	1.8	125
5	TEAL	0.2	—

^aCatalyst **1**, P_{C₂H₄} = 300 psi.

^bDEAC = Et₂AlCl, EADC = EtAlCl₂.

Table 3. Effect of temperature on polymerization^a

Entry	Temp °C	Activity Kg PE/g Ti	T _m °C
1	30	0.4	—
2	60	2.3	128
3	100	9.5	118

^aCatalyst **1**–EASC, P_{C₂H₄} = 300 psi.

Table 4. Effect of pressure on ethylene polymerization^a

Entry	P _{C₂H₄} psi	Solvent	Activity kg			
			PE/g Ti	M _w	PD	T _m °C
1	100	Toluene	3.5	890	1.3	111
2	300	Toluene	9.5	1290	1.5	118
3	500	Toluene	18.3	3200	1.6	119
4	300	Chloro benzene	12.4	1450	1.6	117
5	500	Chloro benzene	24.7	2110	1.7	120

^aCatalyst **1**–EASC, Temp = 100 °C.

Table 5. Influence of solvent on polymerization^a

Entry	Solvent	Activity Kg			
		PE/g Ti	M _w	PD	T _m °C
1	Hexane	0.8	—	—	—
2	Toluene	9.5	1290	1.5	118
3	Chloro benzene	12.4	1550	1.6	117

^aCatalyst **1**–EASC, P_{C₂H₄} = 300 psi.

following equation (33). The branching degree of PEs was determined by taking the value of absorbance of 1378 cm^{-1} peak ($\nu\text{ CH}_3$)

$$\frac{n}{1000C} = \frac{A_{1378}/I\rho - 5.4}{0.691}$$

From the spectrum shown in Figure 2, the reference material indicated a branching degree of 4 compared to 1.4 for the sample. These values are consistent with generally fewer short chain branches (SCB) observed for most linear high density polyethylenes ($\sim 1\text{--}2/1000\text{C}$).

To investigate the molecular properties of polyethylenes further, they were characterized by GPC (Figs. 3 and 4). 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. As mentioned earlier one of the striking feature of these PE's is the exceptionally low molecular weights ($M_w = 840\text{--}1290$) and narrow polydispersities ($PD = 1.4\text{--}1.5$). 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 distributions. The DSC (Fig. 5) 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 (34). The intensity of the equatorial peaks in the X-ray diffractogram (Fig. 6) for the 110 ($2\theta = 21.6^\circ$) and 200 ($2\theta = 24^\circ$) 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

wax samples. A high degree of crystallinity is indicated in all cases, which was generally in the range of 80–88%. The polymer particles are fine and have uniform morphology as seen by Scanning Electron Micrograph. A common feature of these waxes is that the average particle size of polymer as measured during post-reactor work up was typically $< 400\ \mu$. Figure 7 shows SEM's for one of the samples obtained in this study. 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 its end use application.

3.4 Catalytic Pathway

Treatment of mononuclear $\text{Ti}(\text{OR})_4$ type alkoxides with alkylaluminum halides has been reported to yield active intermediates (shown below) responsible for the polymerization of ethylene to low molecular weight products (35, 36).

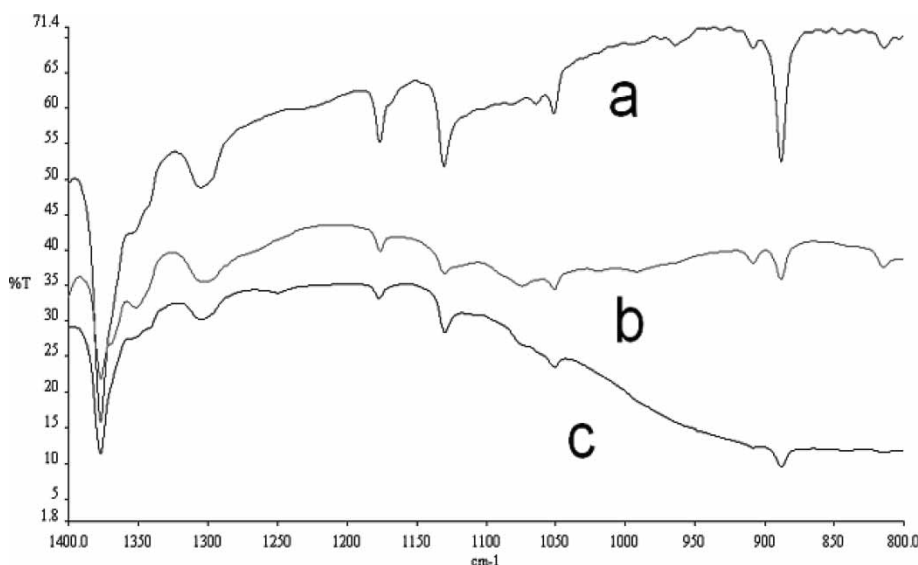
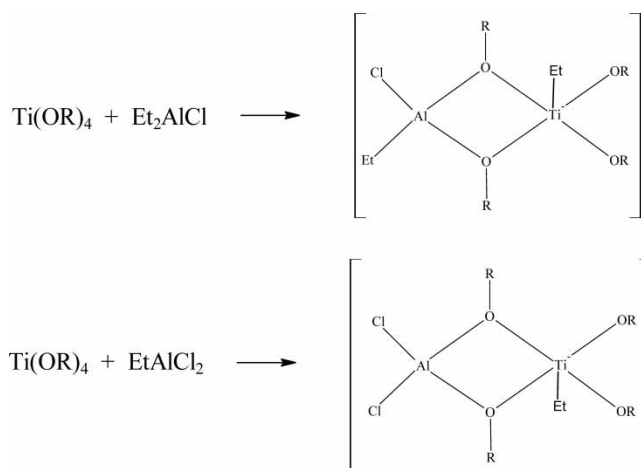


Fig. 2. Fragment of IR spectra for PE sample, (a) commercial sample; (b) Table 1, entry 1; (c) Table 1, entry 2.

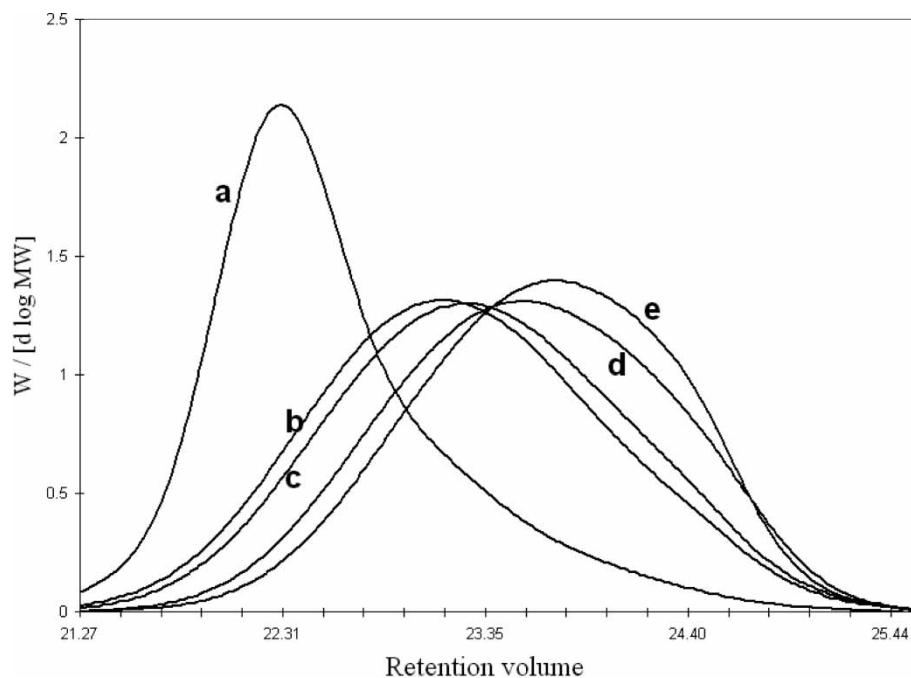


Fig. 3. GPC profile of polymer listed in Table 1, (a) commercial sample; (b) entry 1; (c) entry 2; (d) entry 3; (e) entry 4.

We believe that similar type of active species may be involved in the present Ti-biphenolate system. Moreover, as EASC is derived from an equimolar mixture of EADC and DEAC (37), we have



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-biphenolate catalyst. The reduction of Ti(IV) in presence of EASC will generate catalytically active components.

Qualitative information on the course of reaction was followed with the help of UV-VIS spectrum at different

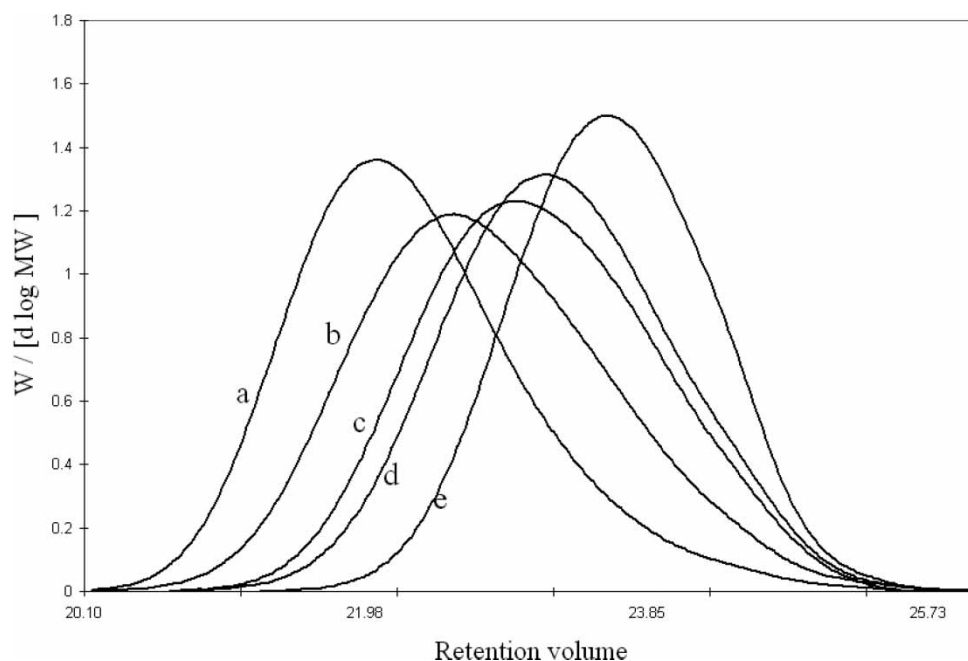


Fig. 4. GPC profile of polymer listed in Table 4, (a) entry 3; (b) entry 5; (c) entry 4; (d) entry 2; (e) entry 1.

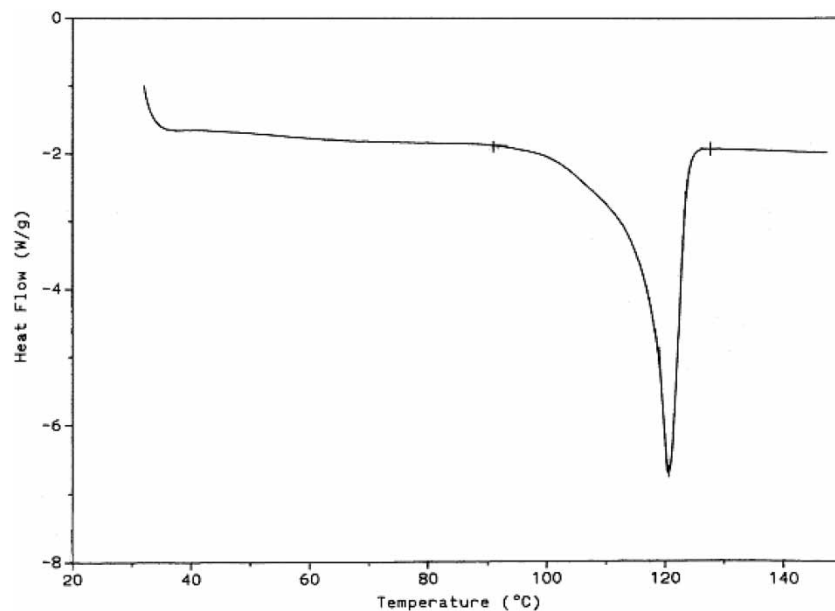


Fig. 5. DSC of PE wax, Table 1, entry 1.

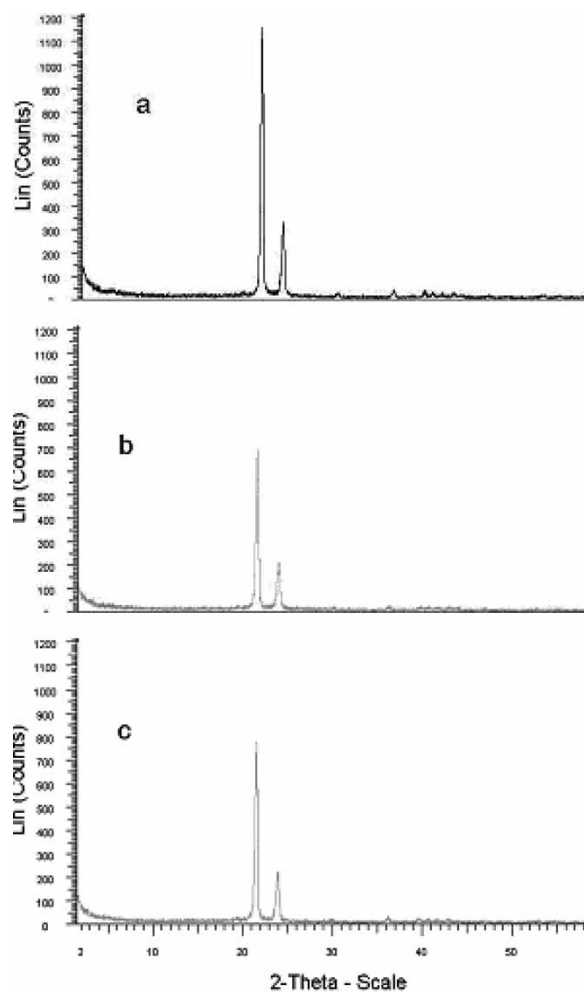


Fig. 6. XRD of PE wax, (a) Table 1, entry 1; (b) Table 1, entry 2; (c) and commercial sample.

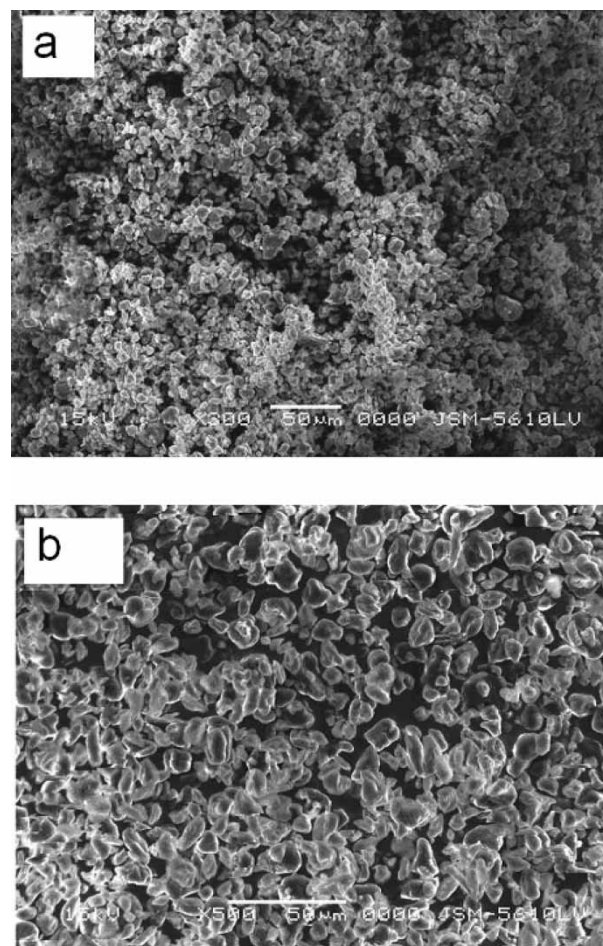


Fig. 7. SEM of PE wax (Table 1, entry 1), (a) $\times 300$ magnification; (b) $\times 500$ magnification.

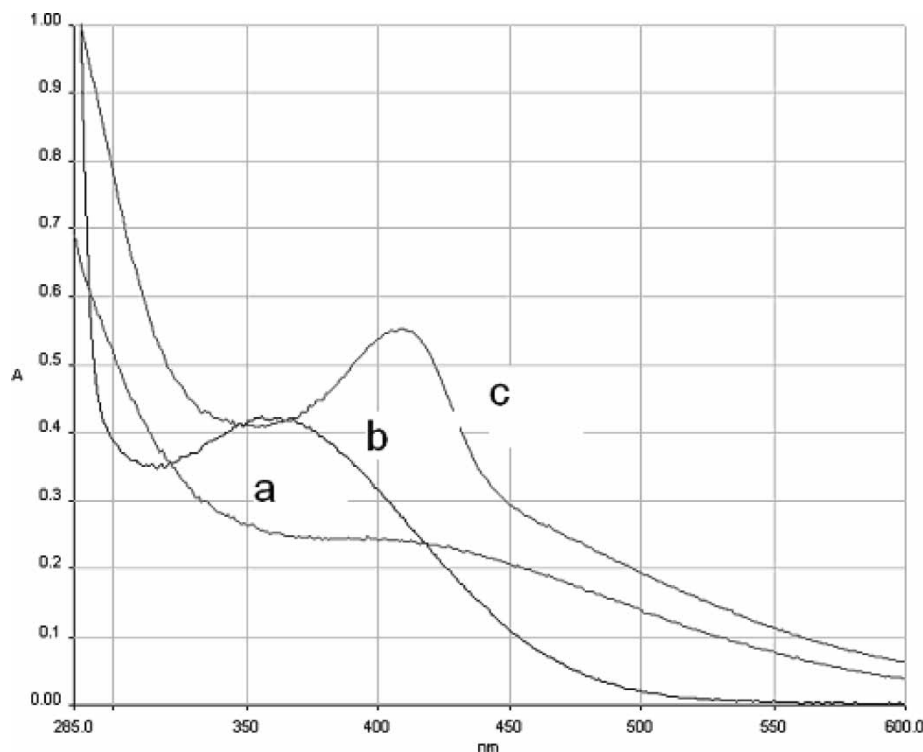
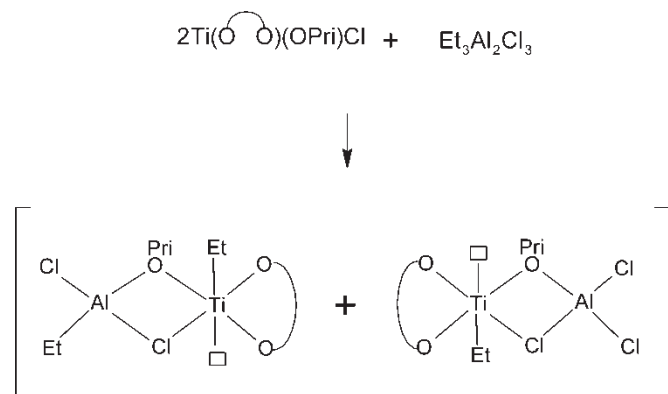


Fig. 8. UV-VIS spectrum (a) Cat **1** + EASC; (b) Cat **1**; (c) Cat **1** + EASC + C₂H₄.

stages of mixing of catalyst precursor and EASC in toluene. For e.g., in Figure 8, the peak at 365 nm after immediate addition of EASC to Ti(O-O)(OPr^t)Cl 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 Cp₂TiCl₂ and MAO by Kaminsky and others (38).

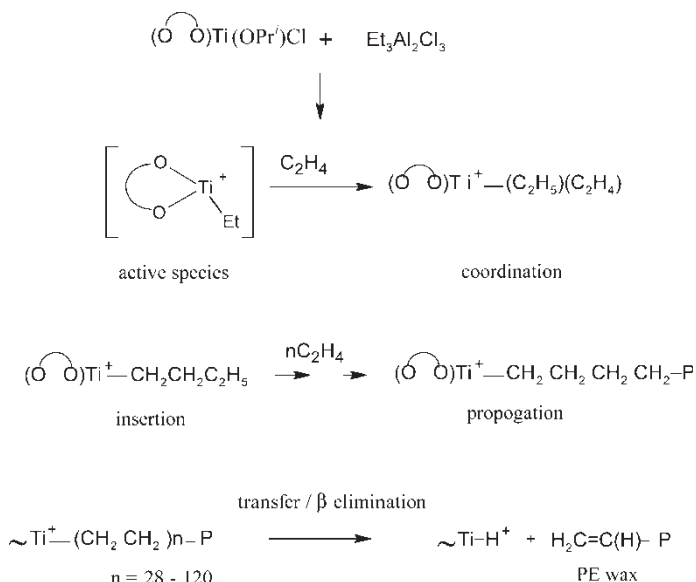
As shown in Scheme 2, the active catalysts in polymerization need to retain monomeric four or five coordinate geometry to allow for olefin insertion and subsequent propagation (39). In the present Ti-biphenolate catalytic system, higher temperatures tend to favor formation of active intermediates responsible for polymerization.



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

3.5 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 is primarily governed by i) nature of linkage between the aryl groups (*viz.* directly bonded C_{phenyl} - C_{phenyl} bond as in **1** and **3** or



Sch. 5. Proposed mechanism of ethylene polymerization by Ti-biphenolates.

separated by CH₂ bridge as in **2** or no linkage as in **4**); ii) type of alkyl aluminum co-catalyst and finally; iii) reaction conditions of polymerization.

Based on a theoretical study by Morokuma (40) 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-biphenolate–EASC catalytic system. The active cationic species generated from the ‘precatalyst’ intermediates shown in Scheme 4 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. Modified Cossee-Arlmann type mechanism (41, 42) can thus be extended to rationalize the polyethylene formation with these catalysts (Scheme 5).

Though chain transfer can occur by other reactions as well, however, the relative inactivity of these catalysts with MAO and Et₃Al indicates that termination is unlikely to proceed by transfer to Al-alkyl or by H₂ under the reaction conditions. It is obvious that steric factors in biphenols and the coordination geometry around the Ti atom contributes significantly towards productivity and *inter alia* molecular weight regulation (43). This implies that the ligands that generate the highest molecular weights do so by slowing down β -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 (13, 40, 44). Efforts are underway to investigate the detailed kinetics of this reaction.

4 Conclusions

The complexes of titanium (IV) with biphenols 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 behaviour of Ti-biphenolate precursors. The close resemblance of polymer properties to commercially important synthetic waxes hold promise for developing alternative cheaper catalysts for this process.

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