

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

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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<sup>^</sup>O)X<sub>2</sub>], 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<sub>40</sub>–C<sub>100</sub>), which are gaining importance for many applications.<sup>1–3</sup> 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.<sup>4,5</sup>

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  $\mu$  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 (Excercex process), use proprietary metallocenes and methyl alumoxane (MAO) as a cocatalyst for the polymerization of ethylene to highly crystalline low-molecular-weight PE.<sup>6–8</sup> 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

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

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.<sup>13–17</sup>

Most of the reported aryl oxides described by the formulation (OR)<sub>*n*</sub>MX<sub>4–*n*</sub> [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.<sup>1,18–22</sup> In a previous work, we showed that under optimum conditions, it is possible to oligomerize ethylene to linear  $\alpha$ -olefins with Ti(IV) aryloxo complexes of monodentate phenols of the type M(OR)<sub>4</sub> in the presence of alkyl aluminum halide cocatalysts other than MAO.<sup>23</sup> 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*<sub>2</sub> symmetric chiral auxiliary ligand, promoted the polymerization of ethylene to a predominantly low-molecular-weight product having a high crystallinity and narrow PD.<sup>24</sup> 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<sub>3</sub>Al<sub>2</sub>Cl<sub>3</sub>) 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 tetrakispropoxide and the different biphenols

were purchased from Aldrich (Milwaukee, WI) and were used without further purification.

### Measurements

Microanalysis was carried out on a PerkinElmer model 2400 instrument. The Ti content in the catalysts was determined gravimetrically as TiO<sub>2</sub>. A PerkinElmer Fourier transform infrared spectrometer (model Spectrum BX) was used to obtain IR spectra of samples pressed into KBr pellets over the 4000 to 400-cm<sup>-1</sup> range. The <sup>1</sup>H-NMR spectra of the catalysts were recorded in CDCl<sub>3</sub> solvent on a Varian NMR 300-MHz spectrometer with tetramethylsilane as an internal reference. FAB mass spectral analysis of catalysts was carried out on a Jeol SX 102/DA-6000 mass spectrometer/data system with 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. Molecular weights of the polymers were determined with size exclusion chromatography. The high-temperature gel permeation chromatography (GPC) analysis of the polymers was carried out with Polymer Lab's PL-GPC 220 chromatograph. A set of three PL Gel 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 before filtration. A sample preparation unit, PL-SP260, was used to dissolve and filter the samples at 135°C. Solutions (0.2%) were injected with the help of an autosampler to record the chromatogram. Viscotek's Trisec conventional software was used to analyze the chromatograms, which were matched with polystyrene calibration curves. The following MHK constants were used to construct a universal calibration curve. For polystyrene,  $K = 1.2105e^{-4}$  and  $a = 707$ ; for PE,  $K = 4.055e^{-4}$  and  $a = 725$ . Differential scanning calorimetry (DSC) was performed under a continuous nitrogen purge on a Mettler-Toledo DSC 822 instrument from 30 to 200°C at a scanning rate of 10°C/min. Indium was used to perform the calibration. Thermogravimetric analysis/differential thermal analysis of the catalysts was recorded in air (heating rate = 10°C/min) from ambient temperature to 600°C on a TA Instruments (Universal V2). The density of the polymers was determined in an *n*-butyl acetate medium at 23°C as per ASTM D 792-00. X-ray experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ , generator voltage = 45 kV, current = 40  $\mu$ A) in the reflection mode, as detected by a scintillation counter. Samples were pressed films approximately 400  $\mu$  thick and were scanned into 2 $\theta$  ranges from 15 to 45° at a rate of 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 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.<sup>25</sup> To a solution of 1 mmol (284.3 mg) of  $\text{Ti}(\text{OPr}^i)_4$  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 ( $\text{C}_{18}\text{H}_{22}\text{O}_4\text{Ti}$ ); C, 61.7%; H, 6.3%; Ti, 13.7%. Found: C, 60.5%; H, 6.6%; Ti, 13.2%.  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ , 300 MHz): 6.96–7.33 (8H aromatic protons), 1.16 (12H,  $\text{CHMe}_2$ ), 3.97 (2H,  $\text{CHMe}_2$ ).

ANAL. Calcd for catalyst 2 ( $\text{C}_{27}\text{H}_{28}\text{O}_4\text{Ti}$ ); C, 69.8%; H, 6.1%; Ti, 10.3%. Found: C, 69.2%; H, 6.1%; Ti, 13.0%.  $^1\text{H-NMR}$ : 6.87–7.83 (12H, aromatic protons), 1.19 (12H,  $\text{CHMe}_2$ ), 3.91 (2H,  $\text{CHMe}_2$ ), 4.48 (2H,  $\text{CH}_2$  bridge).

ANAL. Calcd for catalyst 3 ( $\text{C}_{19}\text{H}_{22}\text{O}_4\text{Cl}_2\text{Ti}$ ); C, 52.7%; H, 5.1%; Ti, 11.1%. Found: C, 53.1%; H, 5.2%; Ti, 11.5%.  $^1\text{H-NMR}$ : 6.96–7.23 (6H, aromatic protons), 1.19 (12H,  $\text{CHMe}_2$ ), 3.79 (2H,  $\text{CHMe}_2$ ), 3.92(2H,  $\text{CH}_2$  bridge).

ANAL. Calcd for catalyst 4 ( $\text{C}_{31}\text{H}_{48}\text{O}_4\text{Ti}$ ); C, 69.9%; H, 9.1%; Ti, 9.0%. Found: C, 69.2%; H, 9.8%; Ti, 9.4%.  $^1\text{H-NMR}$ : 6.98–7.24 (4H, aromatic protons),

1.17 (12H,  $\text{CHMe}_2$ ), 3.96 (2H,  $\text{CHMe}_2$ ), 2.56 (4H,  $\text{CH}_2\text{Me}$ ), 1.22 (6H,  $\text{CH}_2\text{Me}$ ), 1.38(18H,  $^t\text{Bu}$ ).

ANAL. Calcd for catalyst 5 ( $\text{C}_{36}\text{H}_{58}\text{O}_4\text{Ti}$ ); C, 71.7%; H, 9.7%; Ti, 7.9%. Found: C, 72.1%; H, 9.3%; Ti, 7.6%.  $^1\text{H-NMR}$ : 7.13–7.49 (4H, aromatic protons), 1.18 (12H,  $\text{CHMe}_2$ ), 3.50 (2H,  $\text{CHMe}_2$ ), 4.20 (1H,  $\text{CHMe}$ ), 1.67(3H,  $\text{CHMe}$ ), 1.38(36H,  $^t\text{Bu}$ ).

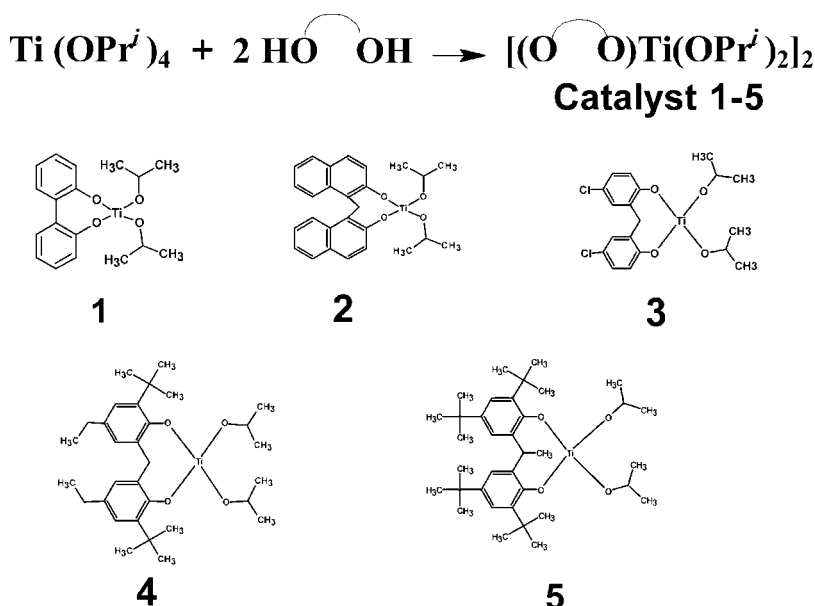
### Ethylene polymerization

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.

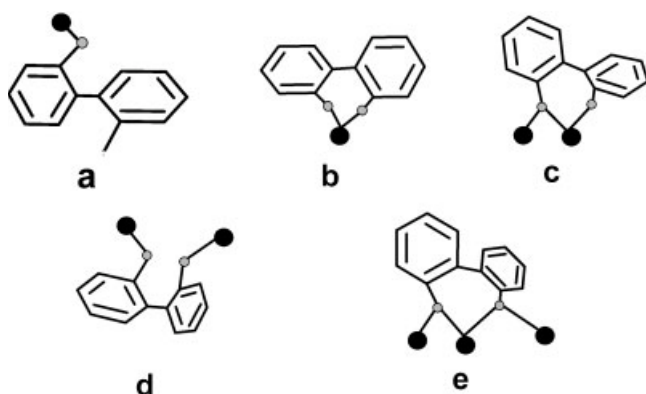
## RESULTS AND DISCUSSION

### 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'-methylene-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<sup>25(b)</sup> as it proved convenient for working with toluene as a solvent for the polymerization of ethylene.

### Catalyst characterization

The stoichiometric reaction between  $\text{Ti}(\text{OPr}^i)_4$  and biphenol ligand in toluene solution afforded dark orange complexes. All of the complexes described by the empirical formulation  $\text{Ti}(\text{Biphenol})(\text{OPr}^i)_2$  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.

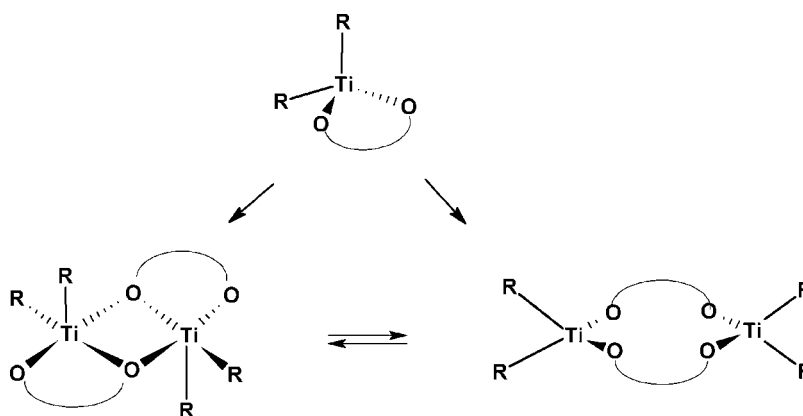
However, the most abundantly formed complexes were those with biphenol in the chelating mode [Scheme 2(b)] and, to a lesser extent, the bridging chelate mode [Scheme 2(c)].<sup>26</sup> In the absence of other ligands, the Lewis acidity of the titanates was enhanced greatly so that coordinative unsaturation

was overcome by the formation of aggregates. Depending on the molar ratio of the starting  $\text{Ti}(\text{OPr}^i)_4$  and the biphenol derivative, a variety of complexes were previously isolated by Heppert, Walsh, and coworkers<sup>27,28</sup> but only a limited number of which were characterized by X-ray crystal structure analysis. Catalysts of type 1 were shown to exist as a dimer in the solid state based on X-ray analysis.<sup>29</sup> Thus, for catalyst 1, we envisaged that the monomeric  $\text{Ti}(\text{O}-\text{O})(\text{OPr}^i)_2$  could undergo facile intermolecular or intramolecular exchange in solution to produce dimeric forms, as indicated by the equilibria shown in Scheme 3 between the two types of species.<sup>30</sup>

With increasing steric bulk of the biphenolate ligands, the tendency to form higher aggregates in the solid diminished. Such phenomena have previously been observed in other Ti-diolate catalysts.<sup>31</sup>

Catalysts 1–5 were characterized by microanalysis, IR,  $^1\text{H-NMR}$ , FAB mass spectroscopy, and thermal analysis. In a typical IR spectra of catalyst 1 and the corresponding biphenol, the low intensity broad peaks in the  $3000\text{--}3500\text{-cm}^{-1}$  region indicated deprotonation of the biphenolate ligand. The  $^1\text{H-NMR}$  spectra were generally simple and were primarily used as a diagnostic tool to ascertain the purity of complexes. A set of multiplets in the region  $7.5\text{--}8.5$  ppm for the aromatic protons was a common feature; in addition, signals due to methyl protons of isopropyl groups ( $1\text{--}1.2$  ppm) were observed. In the FAB mass spectra of catalyst 1, a prominent peak for a ligand fragment (biphenolate ion) appeared at 186. However, the parent ion was not detected, but the highest observed molecular weight ion at 308 was assigned to the  $\text{Ti}(\text{Biphenol})(\text{OPr}^i)^+$  species, which corresponded to the parent ion minus a coordinated alkoxide.<sup>27(a),32</sup>

In general, the higher stability of these catalysts was apparent from the thermal degradation profile, which indicated a single degradation peak around  $480^\circ\text{C}$  assigned to the partial loss of the bulky biphenol ligand. However, complete degradation to the dioxide,  $\text{TiO}_2$ , was not noted up to  $600^\circ\text{C}$  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 <sub>2</sub> TiCl <sub>2</sub>	0.22	—	—	—	—
7	Cp <sub>2</sub> ZrCl <sub>2</sub>	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<sub>2</sub>TiCl<sub>2</sub> and Cp<sub>2</sub>ZrCl<sub>2</sub> 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<sub>2</sub>AlCl) and ethylaluminum dichloride (EADC or EtAlCl<sub>2</sub>), 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<sub>3</sub>Al), 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)<sub>4</sub>, essentially lead to low-molecular-weight linear  $\alpha$ -olefins in the C<sub>4</sub>–C<sub>20</sub> carbon range, in sharp contrast to the exclusive formation of solid PE with sterically bulky bidentate Ti(O<sup>^</sup>O)<sub>2</sub> type complexes used in this study.<sup>23</sup> This can be qualitatively interpreted as chain propagation rates of  $r_p \cong r_t$  in the case of the Ti(OR)<sub>4</sub>-EASC catalyst system, which resulted in oligomer formation, whereas with the Ti(O<sup>^</sup>O)<sub>2</sub>-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 <sup>a</sup>	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

<sup>a</sup> Catalyst 1;  $P_{C_2H_4} = 300$  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;  $P_{C_2H_4} = 300$  psi.

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

Entry	$P_{C_2H_4}$ (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.

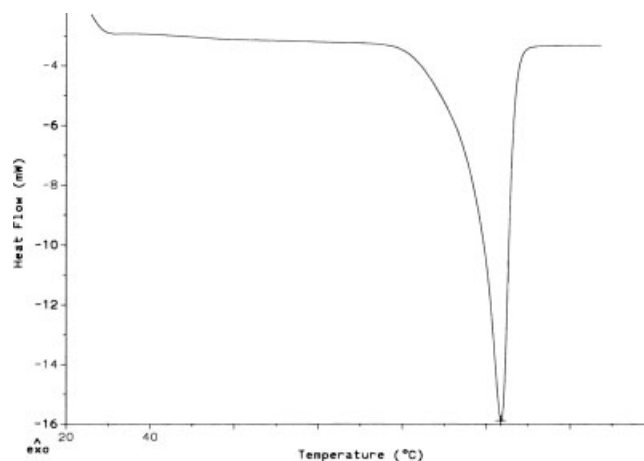
A brief examination of the effects of different solvents (Table V) indicated that chlorinated aromatic solvents, such as chlorobenzene, showed an increase of about 65% in the productivity of PE over that for toluene. Interestingly, this increase was accompanied by a twofold increase in  $M_w$ . However, 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  $\mu\text{m}$ . These and other grades of PE waxes were designed to increase the abrasion resistance and anti-blocking characteristics in flexographic inks and

**TABLE V**  
Influence of Solvent on Polymerization

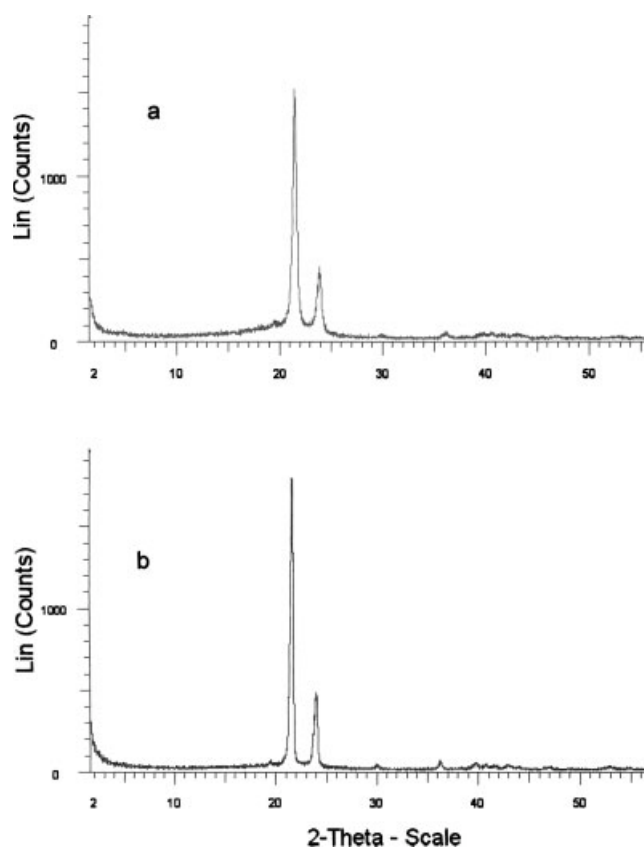
Entry	Solvent	Activity (kg of PE/g of Ti)	$M_w$	PD	$T_m$ (°C)
1	Hexane	0.62	—	—	—
2	Toluene	11.4	1280	1.5	123.4
3	Chlorobenzene	18.8	2520	1.6	121.6

Catalyst 1 EASC;  $P_{C_2H_4} = 300$  psi.

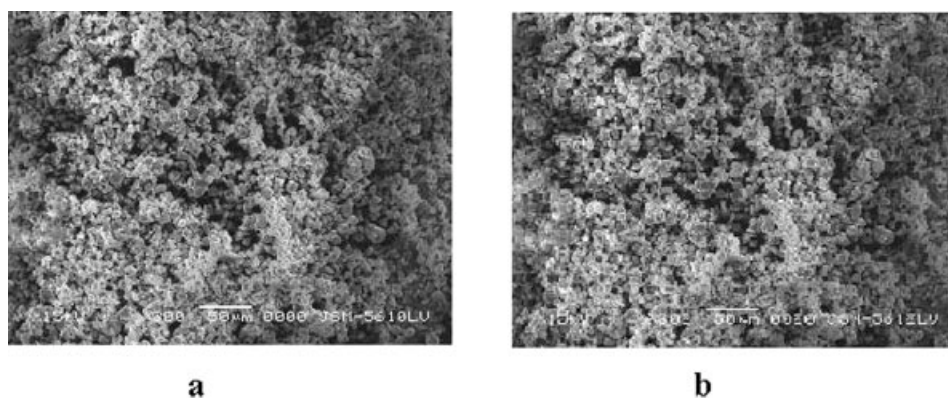


**Figure 1** DSC thermograms of the (a) PE wax and (b) commercial sample (Table I, entry 1).

industrial paints and coatings. More details are available at <http://www.micropowders.com>.]. The intensity of the equatorial peaks in the X-ray diffractogram (Fig. 2) for the 110 ( $2\theta = 21.6^\circ$ ) and 200 ( $2\theta = 24^\circ$ ) reflection planes for the experimental sample closely matched the intensity of the reference sample, and the pattern was indicative of orthorhombic crystallinity in these samples.



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



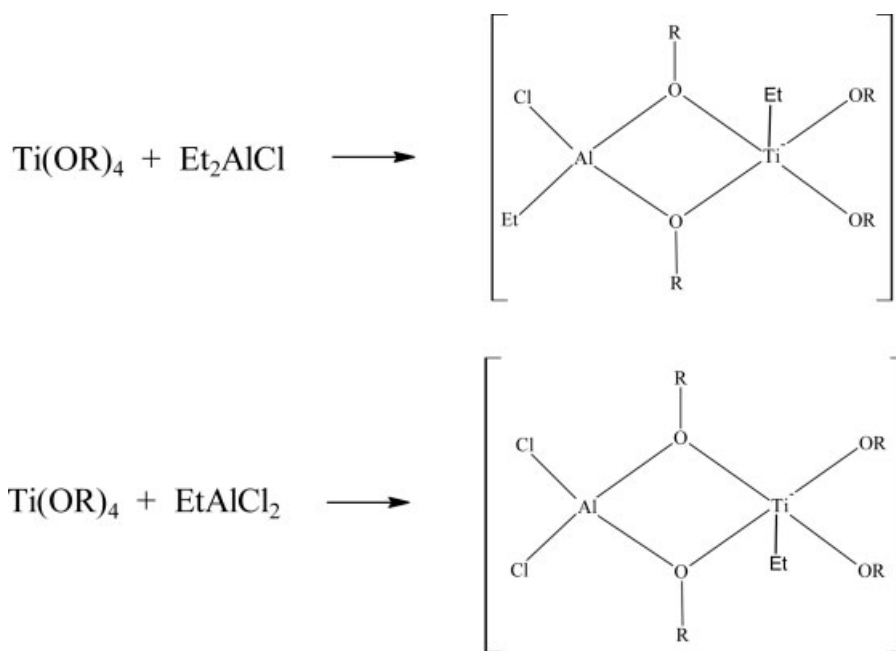
**Figure 3** Scanning electron micrographs of the (a) PE wax (Table I, entry 1) and (b) commercial sample.

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  $\mu$ . In Figure 3, comparative scanning electron micrographs for one of the samples obtained in this study and a com-

mercial 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.<sup>33,34</sup>



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,<sup>35</sup> we have



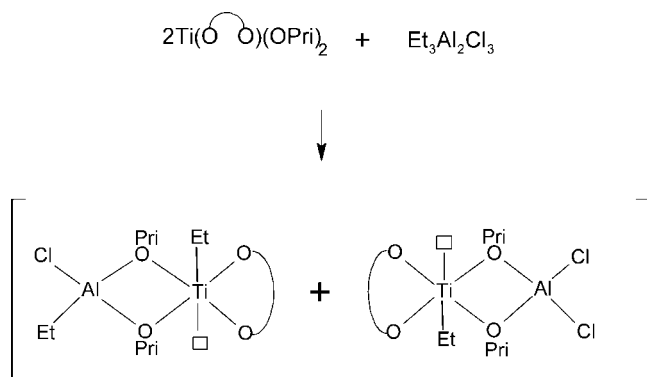
Because EASC could dissociate as DEAC and EADC in solution, it was reasonable to expect the formation

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.<sup>36</sup> In this Ti–biphenolate catalytic system, higher temperatures tended to favor the formation of active intermediates responsible for polymerization.

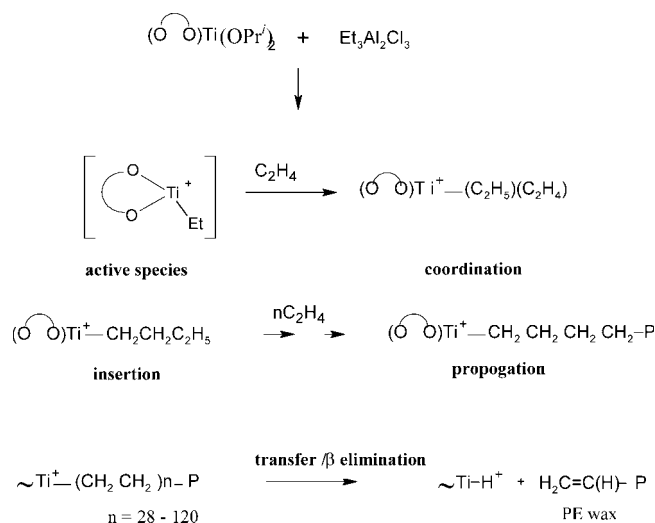
### Mechanistic aspect

On the basis of a theoretical study by Morokuma and coworkers<sup>37</sup> 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.<sup>38,39</sup> 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<sup>40</sup> 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<sub>2</sub> 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<sub>2</sub> 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 polymerization by Ti–biphenolates.

for system 1 (10.7 kcal/mol).<sup>37</sup> Indeed, experimentally, this effect was reflected in higher activities for catalyst 1 compared to catalysts 2–4 (Table I). Interestingly, catalyst 5 showed good activity and behaved similar to catalyst 1. Apparently, in this case, the situation was slightly different due to the extra methyl group in the bridge. Although the bite angle for this ligand was currently not available, it is possible that there was an enhanced Ti–biphenol bridge interaction in this particular case, as seen, for instance, in sulfur bridged biphenols, which thereby favored higher activity due to alteration in the energetics of the O–C<sub>Me</sub>–O–Ti chelate.<sup>41</sup> Furthermore, the polymer molecular weight was highly dependent on the nature of the biphenol ligand within the catalyst precursor. As the bulk of the ligand increased, the polymer molecular weight increased (1200 for catalyst 1 to 3400 for catalyst 2 and ca. 1800 for catalysts 3 and 5). An exception appears to be catalyst 4, which had an unusually lower  $M_w$ , although its activities were much lower than those of catalyst 1. This trend, combined with the effect on productivity of the PE wax (Table I), implied that the ligands that generated the highest molecular weights did so by slowing  $\beta$ -hydrogen abstraction. Although the structure of active intermediates is as yet unknown, the mechanism leading to these linear low-molecular-weight PEs was consistent with those reported previously for solution-phase olefin polymerization with titanium alkoxides and aluminum alkyls.<sup>13,37,42</sup> Efforts are underway to investigate the detailed kinetics of this reaction.

### CONCLUSIONS

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



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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