Chapter 1

Introduction and Background

1.1 Introduction

This introduction briefly traces the chemistry of titanium alkoxides/aryloxides and their application in olefin oligomerization and polymerization. Finally, the need for designing newer titanium complexes for tailoring polyethylenes with desired properties is highlighted.

There has been a resurgence in basic research concerning metal alkoxide / aryloxides due to their potential as precursors in catalytic and stoichiometric organic transformation such as olefin / acetylene metathesis and polymerization [1], in metal oxide nanomaterials [2] etc. However, in conventional catalysis, Titanium alkoxides have been exclusively used as precatalysts in olefin polymerization [3], oxidation [4], epoxidation [5] and C–C bond formation [6]. Dimerization of ethylene to co-monomer grade butene-1, catalyzed by titanium alkoxide-trialkyl aluminum system is one of the earliest processes used in petrochemical industry [7]. Similarly aryloxides of titanium have been shown to be active in oligomerization of ethylene to linear alpha olefins (C_4-C_{30} alkenes) in presence of alkyl aluminum co-catalyst [8].

Metal alkoxides / aryloxides are generally represented as $[M(OR)_x]_n$ where M = metal of valency x ; R = alkyl, substituted alkyl or aryl group and n = degree of molecular association. Solubility and volatility are the two key properties of metal alkoxides which provide convenient methods for their purification as well as making them suitable as precursors for catalytic activity. Titanium alkoxides are in general highly moisture and air sensitive. Stringent precautions are therefore essential during their synthesis and handling.

Preparation : There are three main synthetic routes to the preparation of titanium alkoxides :

1. Stoichiometric reaction between titanium tetraisopropoxide and a higher boiling alcohol or phenol by an alcohol exchange and separation of liberated *iso*-propanol by azeotropic / vacuum distillation [9].

$$\mathbf{Ti(OPr^{i})_4 + 4ROH \longrightarrow Ti(OR)_4 + 4Pr^{i}OH \uparrow}$$

2. Treatment of a lithium salt of phenol with titanium tetrachloride followed by removal of LiCl [10].

$$\mathbf{TiCl_4 + 4LiOR \longrightarrow Ti(OR)_4 + 4LiCl \downarrow}$$

3. Low temperature reaction between the phenolic ligand and titanium tetrachloride in presence of a base (usually tertiary amine) for eliminating the HCl formed [11].

$$\mathbf{TiCl_4 + 4ROH \xrightarrow[-4HCl]{Et_3N} Ti(OR)_4}$$

One of the characteristics feature of metal alkoxides is their ability to exchange an alkoxide group with alcohol that has been greatly exploited for the synthesis of a variety of derivatives [12].

$$\mathbf{M(OR)_x + nR'OH \longrightarrow M(OR)_{x-n}(OR')_n + nROH \uparrow}$$

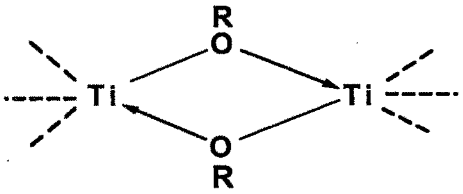
In the above illustration if the alcohol, R'OH has a higher boiling point than ROH then the desired product can easily be obtained by shifting the equilibrium by removing ROH, preferably as an azeotrope eg. with benzene by fractional distillation. Many of the final products prepared by this route assume special significance because of their reduced molecularity, enhanced solubility (in organic solvent) and volatility as well as novelty in structural features.

The physical properties of titanium alkoxides are largely influenced by the size and shape of the alkyl group. Owing to the high electronegativity of oxygen (3.5 on Pauling scale) the Ti-OR bonds would be expected to possess significant ionic character. Thus Ti - oxygen bond ($M^{\delta+}$-$O^{\delta-}$-C) in titanium alkoxide could be expected to possess around 65 % ionic character. The factors that have been postulated to explain the attenuation in the polarity of Ti – O bond are :-

(1) The inductive effect of the alkyl group on the oxygen atom which increases with branching of the alkyl chain.

(2) The presence of oxygen *p* to metal dπ bonding for early transition metals.

(3) The formation of oligomeric species through alkoxy bridge of the type :



This latter tendency which leads to coordination polymerization is a dominant feature of metal alkoxide unless inhibited by steric and electronic factor [13]. Bradley, Mehrotra and Wardlaw [14] have tried to analyze steric and electronic factors for alkoxy derivatives. Results indicate that the extent of aggregation for an appropriate stoichiometry is dependent on the following consideration.

1) Aggregation increases as the metal atom becomes more electron deficient.
2) Larger the size of metal atom greater the tendency to increase the degree of association (n) by forming alkoxo bridged systems.

The steric effect of the alkyl substitutions which, with increasing steric demand, inhibit aggregation have been found to be of greater importance than the electronic nature of the substituents in determining the ultimate extent of aggregation.

Despite the abundance of aryloxide ligands there are relatively few examples of chelating bis(aryloxide) ligands [10,15]. Sterically hindered biphenols and chelating biphenols possess C_2 symmetry and can provide a stereochemically rigid framework for the metal center. They should therefore afford appropriate spatial framework necessary for stereospecific transformation, including the stereoregular polymerization of olefins. Furthermore, their chelating nature inhibits the possible disproportionation reaction in complexes of the type LL^1MX_2 ($M = Ti$, L, $L^1 \neq Cp$). Sterically hindered auxiliary group on the binaphtholate and biphenolates allow an extended degree of shielding that can be tuned without significantly altering the electronic characteristics of ligands. The application of such a catalyst should aid in polymerization of olefins with well defined polymer microstructure.

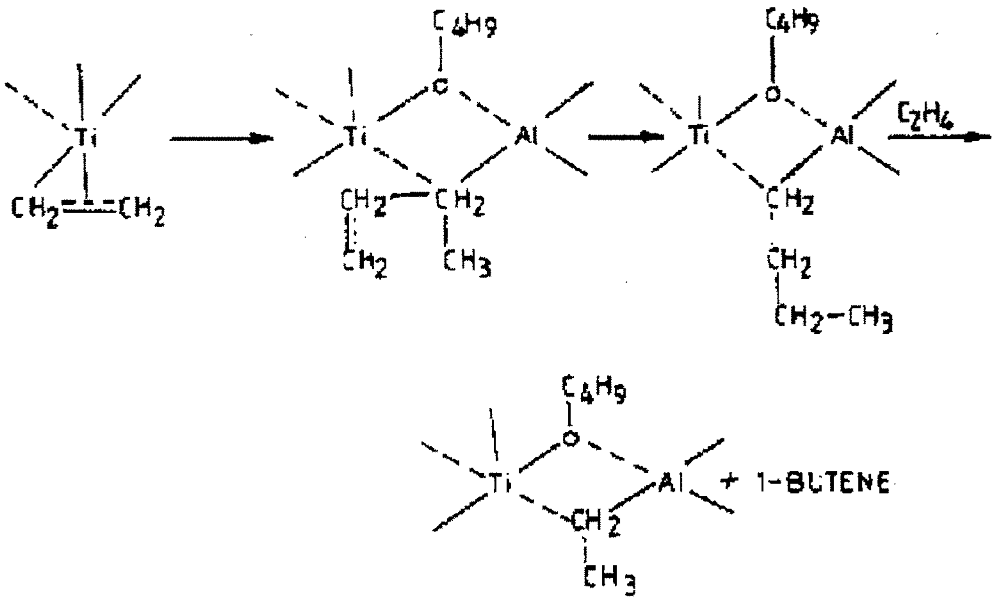
1.2 Titanium Alkoxide in Ethylene Oligomerization and Polymerization

Dimerization of ethylene

Titanium alkoxides with alkylaluminum compounds (Table 1.1) are known to be good catalysts for ethylene dimerization to give selectively butene-1

$$2CH_2{=}CH_2 \xrightarrow{\text{Cat}} H_3C\text{-}CH_2\text{-}CH{=}CH_2$$

A mixture of titanium esters and trialkyl aluminum also produce butene from ethylene [16]. Zhukov and coworkers [17] have reported optimum conditions for the dimerization of ethylene using titanium alkoxides. Another report [18] claims that dimerzation of ethylene was favoured when the ratio of AlR_3 / $Ti(OR)_4$ was < 10. The physiochemical aspects of catalytic system have been investigated in detail [19]. When the dimerization was carried out with a mixture of ethylene-hydrogen at a H_2 concentration of 5-95 % by volume the result was enhanced 1-butene formation [19g]. It has been reported that with the use of $AlEt_3$-$Ti(OBu^n)_4$ the conversion to the dimer is maximum for an Al:Ti ratio of 4:1. The activity can be increased by the addition of triphenylphosphine or phenylacetylene [20]. Angelescu and co-workers [20a] proposed following mechanism (scheme 1.1) for dimerization of ethylene on the bimetallic titanium-aluminum complex whereas Cossee [21] originally proposed a monometallic mechanism for the $Ti(OMe)_4$-$AlEt_3$ system.



Scheme 1.1 Dimerization of Ethylene on Bimetallic Titanium-Aluminum Complex.

Detailed reports [22] on the kinetics and mechanism of ethylene dimerization by the $Ti(OR)_4$-AlR_3 systems in various solvents are available [22-24]. 1-Butene is generally formed by a β-hydride abstraction, a common cleavage reaction of transition metal-carbon bond [25]. The β-hydrogen of the alkyl group attached to the metal is transferred to the latter with formation of metal hydride and the organic residue leaves the metal center as vinylic olefin [26]. The ease of β-hydrogen abstraction depends on the metal, its valency and the ligand environment.

In Table 1.1 is summarized some representative examples of ethylene dimerization by $Ti(OR)_n$ catalysts.

Table 1.1 Selected studies in Dimerization of Ethylene by Titanium aryl/alkoxides.

Catalyst System	Reaction condition	Products	Comments	Ref.
$Ti(OR)_4 - (C_2H_5)_3Al$		1-butene (60-90 %), 2-butene	--	16
$Ti(OR)_4 - (C_2H_5)_3Al$	Toluene or n-heptane, 20°C	1-butene	Ti/Al = 10, selectivity = 98.9 %	27, 22(c)
$Ti(O\text{-}i\text{-}Pr)_4\text{-}Al(C_2H_5)_3$	n-heptane, 7.12 atm. 90°C, 120 min	1-butene (>90 %), 2- butene (~1.5%), hexane (2-4%), polyethylene	Al/Ti = 5.6; butene-1 yield = 720g/g of cat.	28
$Ti(OR)_4\text{-}R_3Al$-electron donor additive	Polar solvent	1-butene	Selectivity is high with polar solvents and electron donor additives	22(d)
$Ti(OBu)_4\text{-}(CH_3)_3Al$	Deuterated ethylene	1-butene, deuterated butenes	--	29
$Ti(OR)_4\text{-}R^1{}_3Al$ (R= Bu, Pr, pentyl, phenyl ; R^1 = isobutyl, propyl, ethyl)	---	1-butene	Activity of cat. follows the order R = butyl > pentyl > propyl > isopentyl > phenyl , selectivity of the catalyst is in the reverse order.	19(f), 30, 31
$(BuO)_nTi(ac)_{4-n}$ (n =2,3); ac = acetylacetonato) / $TiCl_4\text{-}(CH_3)_3Al_2Cl_3$	CH_2Cl_2 or toluene, n-heptane , 100°C	1-butene (65 %), hexene (35 %)	Order of reactivity is halogenated hydrocarbons > aromatic hydrocarbons > aliphatic hydrocarbons.	32

Oligomerization of Ethylene

Last two decades have witnessed increasing importance of higher linear C_{6-20} α-olefins which are a source of biodegradable detergents, new kind of polymers, lubricants and many other industrially useful chemicals. Alpha olefins are generally obtained through thermal or catalytic cracking of paraffins, oligomerization of ethylene, dehydrogenation of paraffins, dimerization and metathesis of olefins, dehydrogenation of alcohols and electrolysis of C_{3-30} straight chain carboxylic acids. The most desirable ethylene oligomeriztion products are those for which $n < 20$. The reaction occurs only in presence of a catalyst. Catalytic cycle for this reaction comprises of two steps :-

1) Chain growth (propagation) step

$$\mathbf{Cat\ R + H_2C = CH_2 \longrightarrow Cat\ CH_2 - CH_2\text{-}R} \qquad \text{-------}\ (1)$$

and

2) Hydrogen elimination from β carbon to the catalyst center

$$\mathbf{Cat - H_2C\text{-}CH_2 - R \longrightarrow Cat - H + CH_2 = CHR} \qquad \text{-------}\ (2)$$

Complexes of titanium are the most used catalysts for ethylene oligomerization. Alkoxy derivatives of titanium modified with organoaluminum compounds particularly with cholroalkylaluminum are active in ethylene oligomerization (Table 1.2).

This reaction takes place *via* :-

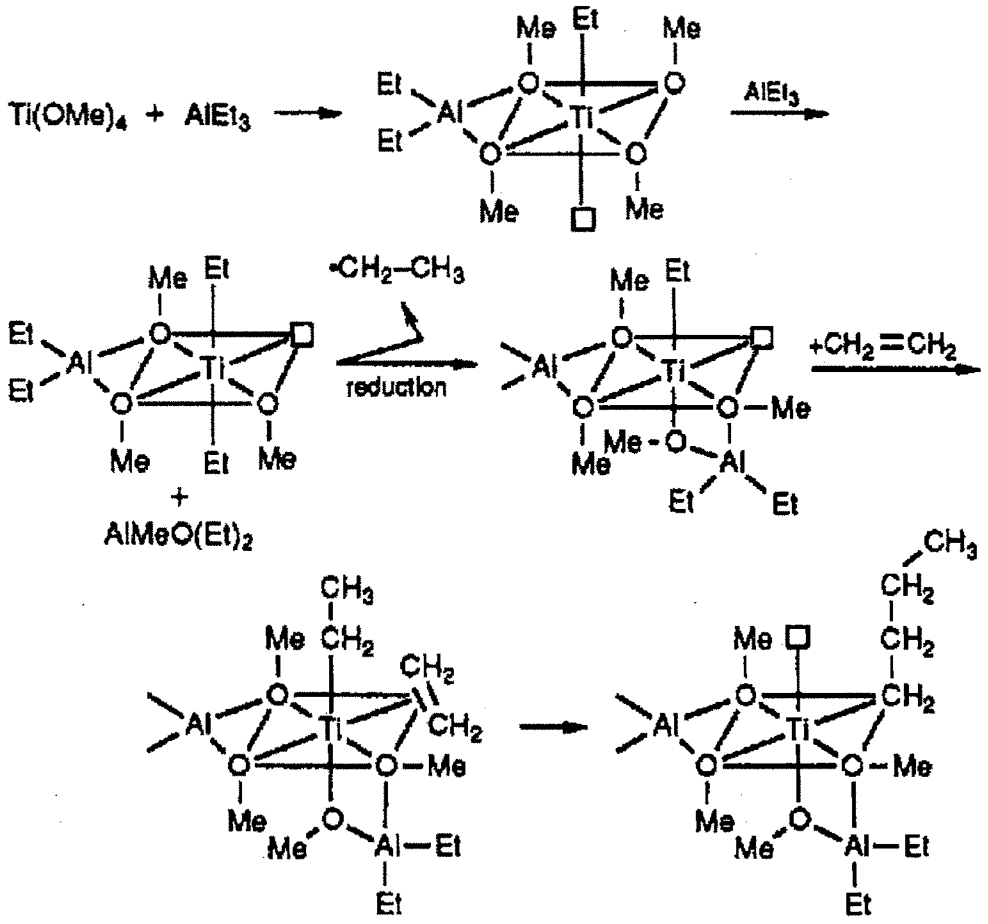
(1) Active center formation

(2) Olefin coordination on the titanium ion

(3) Chain propagation

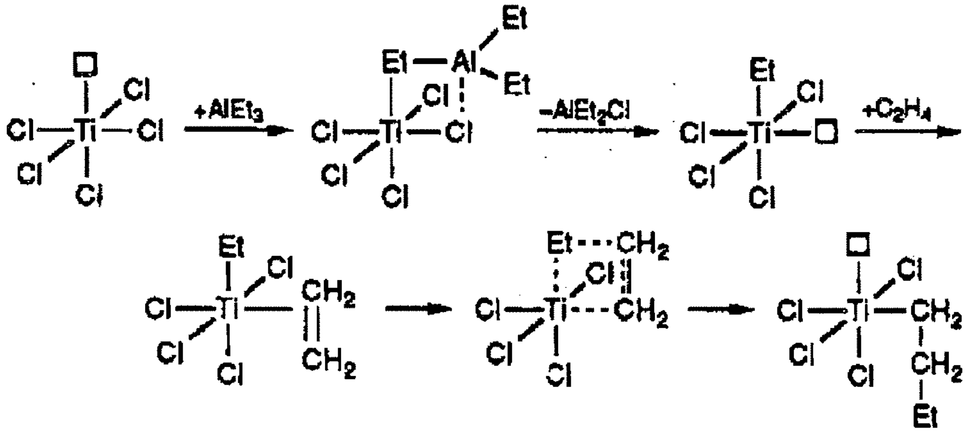
(4) Termination of the chain growth

The olefin oligomerization mechanism on bimetallic center proposed by Rodriguez and Looy [33] is presented in scheme 1.2. In this example the first step of the reaction is alkylation of the titanium center. Next ethylene is coordinated to the titanium center. This is the cause of weakness of the Ti-C bond.



Scheme 1.2 Bimetallic Mechanism of Ethylene Oligomerization.

In case of the monometallic mechanism postulated by Cossee and Arlman [21, 34] the olefin insertion occurs *via* four center intermediate (scheme 1.3). The ethylene oligomerization is initiated here only with titanium ion and its ligands.



Scheme 1.3 Cossee-Arlman Monometallic Mechanism of Ethylene Oligomer Chain growth.

In Table 1.2 is compiled selected examples of ethylene oligomerization by Ti-alkoxides.

Table 1.2 Selected studies in Oligomerization of Ethylene by Titanium aryl/alkoxides

Catalyst	Reaction condition	Products	Yield	Ref.
$(C_2H_5O)_3TiCl$/ $C_2H_5AlCl_2$	Toluene, 12 atm, -20 to 0°C, 1 Hr.	Olefins $C_8 = 32$ % (α-olefins), $C_{10\text{-}50} = 67.1$ %, (∝ olefins = 85%), $M_n = 153$	10-15 mol of C_2H_4 (g of catalyst)$^{-1}$ h^{-1}, ethylene conv = 82 %	26, 35, 36
$(CH_3O)_4Ti$/ $(C_2H_5)_3Al$	12 Kg/cm^2, 40°C	Olefins $C_4 = 73$ %, C6 = 26 %, ∝ olefins = 100 %	Ethylene conv = 82 %	37
$(BuO)_4Ti$/ $(C_2H_5)_3Al$	n-heptane, H_2, and C_2H_4 mixture, 2.5 atm, 57 °C, 1h	Olefins $C_4 = 77.6$ %, $C_6 = 22.0$ %, PE = 0.4%	--	38

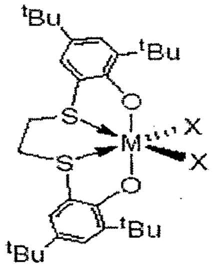
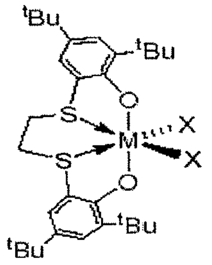
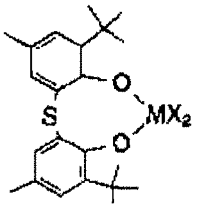
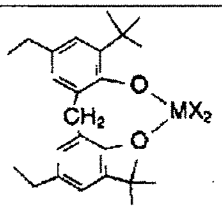
Olefin Polymerization :

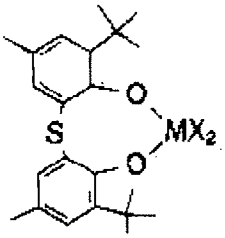
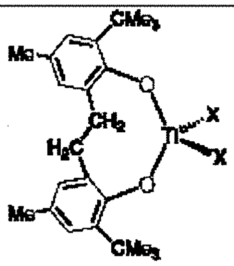
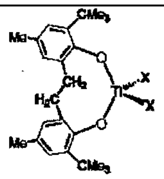
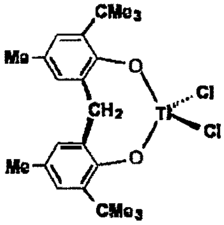
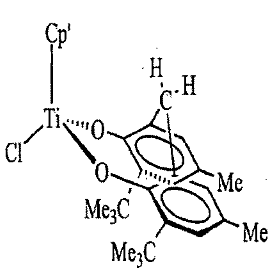
Recently titanium complexes with chelating biphenolate ligands have attracted attention as possible catalyst in α–olefin polymerization. When activated with methylalumoxane, some of these complexes afforded ethylene/styrene copolymerization. Such ligands not only are more easily accessible than cyclopentadienyl ligands but the complexes derived therefrom also allow access to novel types of polymers.

Schaverian et. al [40] have studied sterically hindered binaphtholates. Titanium complexes formulated as S(4-Me, 6-Bu $C_6H_2)_2TiCl_2$ has been reported to be highly active for alpha olefin polymerization [11]. Mülhaupt and Okuda [41] have investigated the ethylene-styrene copolymerization using bis(phenolate) complexes of titanium using methylalumoxane (MAO) as cocatalyst. Aida et.al have studied polymerization of ε-caprolactone using Ti–complexes of 2,2' methylene bis(6-*tert*-butyl-4-methylphenol). Cuenca [43] has studied similar type of complexes with Cp as one of the anciliary ligand for propylene and styrene polymerization. Recently Okuda et al [39] have studied biphenolate $\{TiCl_2(OC_6H_2Bu^t{}_2\text{-}4,6)_2S)\}$ for styrene polymerization. It was demonstrated that ethylene*bis*-2,2'(6-*tert*-butyl-4-methylphenol) is useful in polymerization of ethylene when bound to titanium.

A selection of titanium complexes containing chelating biphenolates as olefin polymerization catalysts is shown in Table 1.3.

Table 1.3 Selected studies in Polymerization of olefins by Titanium aryloxides

Catalyst	**Reaction condition**	**Products**	**Ref**
 $MX_2 = TiCl_2$	Al:Ti ratio=1500, toluene, Temp = 40°C, monomer = styrene	Polystyrene, $T_m = 223°C$, $M_n = 265 \times 10^{-4}$, PD=2	39
 $MX_2 = Ti(OPr^i)_2$	Al : Ti ratio =1500, toluene, temp = 40°C, monomer = styrene	Polystyrene, $T_m = 223°C$, $M_n = 172 \times 10^{-4}$, PD=1.8	39
 $MX_2=TiCl_2$	5 min, 20°C, 500 equi. MAO, toluene monomer = ethylene	Polyethylene, $M_w = 3.5 \times 10^5$, PD = 11.9	40
 $MX_2=TiCl_2$	30 min, 20°C, 500 equi MAO, toluene monomer = ethylene	Polyethylene	40

 MX_2=$TiCl_2$	MAO co-catalyst monomer = hexene	Atactic polyhexene, M_w = 7800, PD = 1.8	40
 X = Cl	Monomer = ethylene + styrene toluene, 60^{0}C, 1h, styrene/ethylene molar ratio = 5/1, MAO, Al : Ti ratio = 1000	ethylene- styrene copolymer	41, 42
 X=(OPr^i)	toluene, 60^{0}C, 1h, styrene/ethylene molar ratio = 5/1, MAO, Al:Ti ratio = 1000	Ethylene-styrene copolymer	41, 42
	toluene, 60^{0}C, 1h, styrene/ethylene molar ratio= 5/1, MAO, Al:Ti ratio = 1000	Ethylene- styrene copolymer	41, 42
	Monomer = propylene Time = 12 min, MAO co-catalyst	polypropylene, M_w = 3.2 x 10^{-4} PD=1.8, T_m= 93°C	43

1.3 Polyethylene types and their application :

In the mid 1950's Karl Ziegler and Giulio Natta reported the first stereo regular polymerization of ethylene [44-45]. These discoveries spearheaded the synthesis of a host of new materials and revolutionized the polyolefin industry. Polyethylene is now one of the most common plastics in the world. It is used to make grocery bags, bottles, children's toys and a most of other everyday items. Polyethylene is of great industrial importance and is produced in millions of tons each year. The production of this material has the greatest growth rate of 11.2 % per year and is believed it will replace other plastics on the market in future [46-47]. Its versatility combined with its physical and chemical properties makes it an attractive commodity to produce.

Several desirable applications can be obtained by choosing one of a large variety of polyethylene grades. Microstructural properties such as molecular weight, molecular weight distribution, branching structure and stereoregularity determine the end application of polyethylenes. The choice of polymer depends on the desired properties such as its stiffness, toughness, stress-crack resistance, optical clarity etc. and the polymer processing operation to be used.

Depending on the microstructural and physical properties of polyethylene it is generally categorized by the of following types:

High Density Polyethylene (HDPE)

High density polyethylene is manufactured by solution, slurry and gas-phase polymerization using a transition metal based catalyst. Process conditions are; temperature 140-150°C and ethylene pressure of about 8 Mpa for the solution process, 70-150°C ethylene pressures of about 2-5 Mpa for the slurry and gas-phase processes. Density lies in the range of 0.940 to 0.960 g/cm^3. It is a linear, semicrystalline ethylene homopolymer

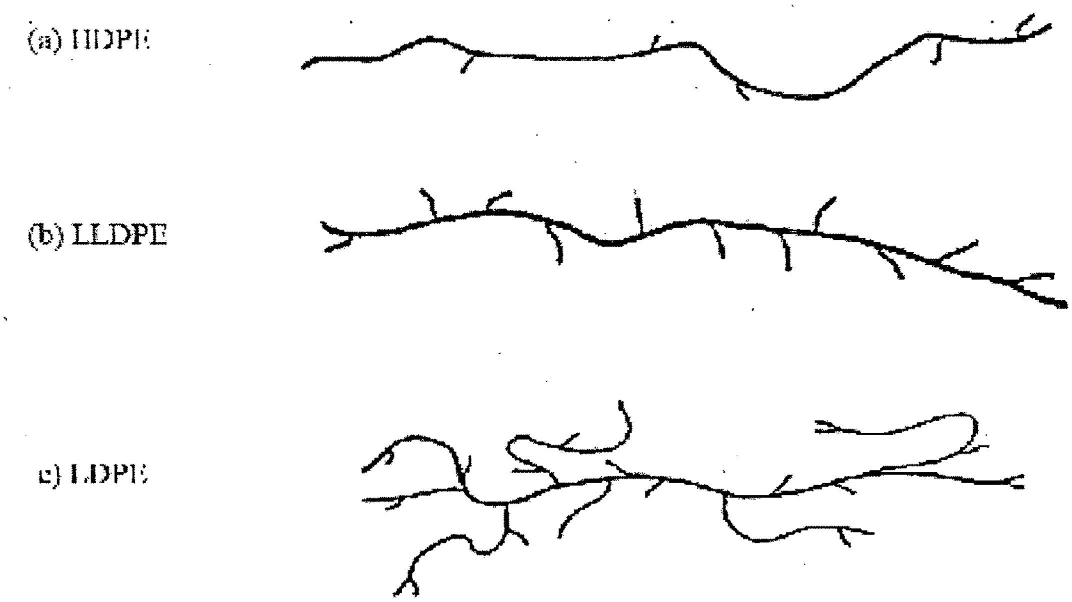
(T_m=135°C) prepared by Ziegler–Natta and Chromium based coordination polymerization technology.

Low Density Polyethylene (LDPE)

Low density polyethylene is produced by a high pressure, free-radical polymerization process first discovered by Imperial Chemical Industries in the UK in 1933. The process conditions are ethylene at a pressure of 120 – 300 Mpa, temperature of 130-350°C and a very short residence time from 15 sec. to 2 min. dependant on the reactor type. The reactor might be tubular or a stirred autoclave. These are random copolymer of ethylene and alpha olefins (e.g. 1-hexene, 1-butene or 1-octene) with densities from 0.915 to 0.930 g/cm^3 containing short and long branches formed during the synthesis. It is produced commercially using Ziegler-Natta, Chromium and metallocene catalyst.

Linear Low Density Polyethylene (LLDPE)

Linear low density polyethylenes are α-olefin copolymers, usually with 1-butene, 1-hexene or 1-octene with densities of 0.915-0.940 g/cm^3. While LDPE contains both long and short-chain branches, LLDPE contains only short chain branches. The LLDPE is produced using the same slurry and gas phase processes as for HDPE manufacturing but with the addition of ~ 4 – 8 mol % of a co-monomer.



Ultra High Molecular Weight PolyEthylene (UHWPE)

Polyethylene with molecular weights in the range of 4-10 millions is referred as ultra-high molecular weight polyethylene or UHMWPE. This material is used to manufacture fibers of such high tensile strength that they can replace Kevlar, typically used in bulletproof vests.

Ultra Low Molecular Weight PolyEthylene (ULWPE)

Polyethylene with molecular weight in the range of 1000 to 3000 is referred as ultra low molecular weight polyethylene also as PE wax. 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 [48]. 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 [49-50].

1.4 Scope and Aim of Present Work :

Based on the aforementioned background material, there is clearly a vast potential to be exploited in the organometallic chemistry of titanium biphenolates. Hence, the objective of the present work are:

- To synthesize new titanium complexes derived from chiral and achiral biphenol precursor ligands.
- To develop a general methodology for isolation and characterization of relatively stable and inexpensive non-metallocene catalyst precursors.
- To investigate the reactivity of these titanium-biphenolates and related aryloxides in polymerization of ethylene and other substrates.

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