

Chapter I: Introduction and Background

1.1 Introduction

Polyolefins are polymers produced from simple olefins (alkenes) as monomers. They are considered “commodity polymers” and are the most widely produced plastics in the world. There are many types of polyolefins. However, commercial polyolefins are polyethylene (PE), polypropylene (PP), polystyrene (PS), acrylonitrile butadiene styrene (ABS), polyvinylchloride (PVC), and polyethylene terephthalate (PET).

Worldwide plastics industry witnessed a steady growth over the past years, which is reflected in the increased consumption figures of all types of plastics material. This increase in plastic and polymer consumption is expected to continue with an average growth of 5% each year until 2015. Figure 1.1 below shows the chart of 2007 world-wide polyolefins consumption [1].

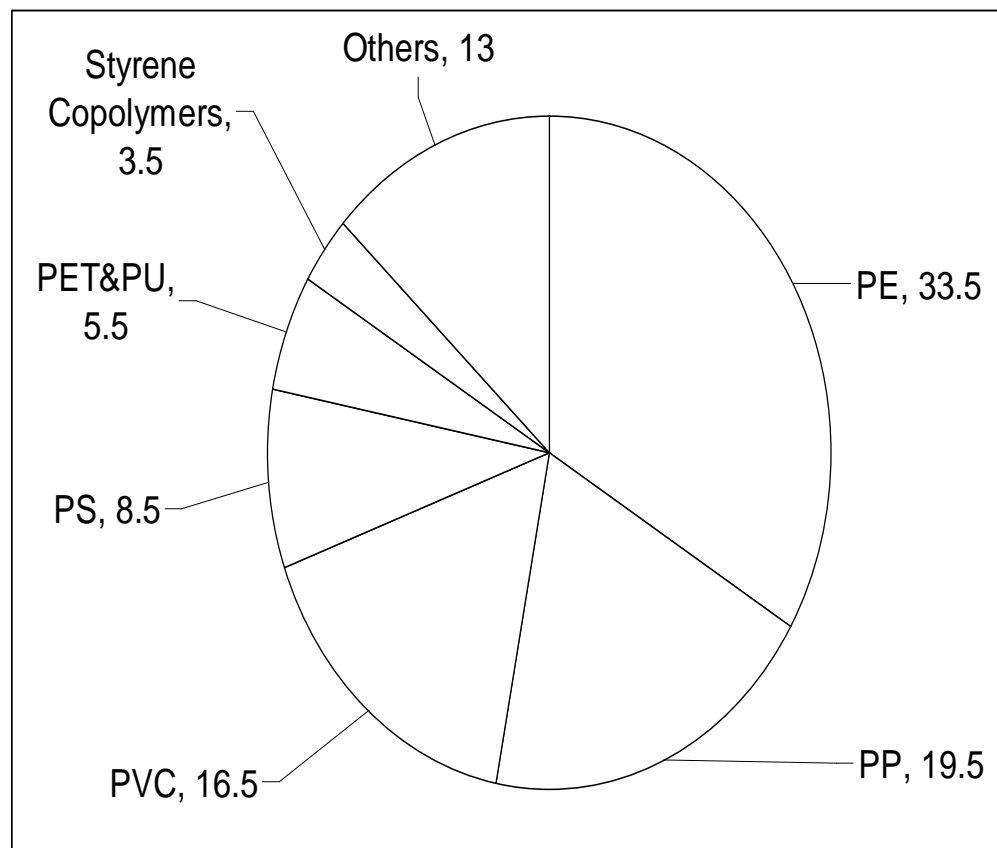


Figure 1.1: 2007 consumption of plastics in the world [1], values in percentage (%)

Polyethylene (PE) is now one of the most common plastics in the world. Because of its versatility combined with its physical and chemical properties, PE is an attractive commodity to produce. It is of great industrial importance and is produced in millions of tons each year. Furthermore, its world demand is about 34% of the yearly total world demand for thermoplastic. In addition, global polyethylene demand is estimated to grow annually through 2020 with an average 4.4% which is about 1% above the expected global gross domestic product (GDP) growth. The global PE demand in terms of 1000 tons per year up to 2020 is projected in Figure 1.2 [1].

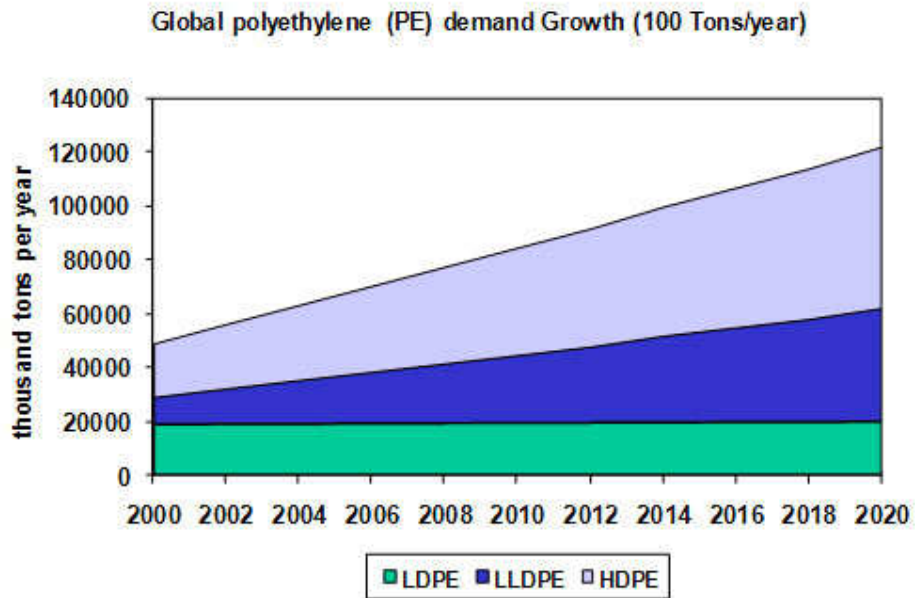


Figure 1.2: Projected world PE demand up to 2020 [1]

The polyethylene molecule has the basic structure of $-(\text{CH}_2\text{CH}_2)_n-$, which consists of a long chain repeated ethylene units. Even though its structure is very simple, there are several types of polyethylene with different branching structures.

1.2 Types of polyethylene

1.2.1 Low density polyethylene (LDPE)

Low density polyethylene (LDPE) is a highly branched polyethylene which was first discovered in 1935 by Perrin of ICI laboratory. While working, he found that ethylene could be prepared by free radical polymerization at very high pressure (600-3500 bar) and high temperature (200-350°C) as a semi crystalline solid. This discovery, led to the commercialization [2] of LDPE in 1938. Beside the fact that LDPE is highly branched, it is a soft, flexible and transparent polymer with low crystallinity (45-65%) and a density of between 0.915 and 0.935 g/cm³. It also has low tensile strength. LDPE finds wide application in the wire and cable industry and in the film or packaging industry. Even though LDPE is being replaced by LLDPE resins, it is still widely favored for its good processability and high melt strength due to the entanglement of the branches [3].

1.2.2 Linear low density polyethylene (LLDPE)

Produced by copolymerization of ethylene with a small amount of α -olefins (1-butene, 1-hexene and 1-octene), LLDPE has similar properties with low density polyethylene (LDPE). It forms translucent films that are fairly flexible with good mechanical properties. Its demand is gradually growing and it is replacing the LDPE because of its better conditions for production (pressure \approx 20 atm and temperature \approx 80°C) [4, 5]. LLDPE is used for plastic bags, sheets (where there is a need of lower thickness than traditional LDPE), plastic wrap, stretch wrap, pouches, toys, lids, pipes, buckets and containers.


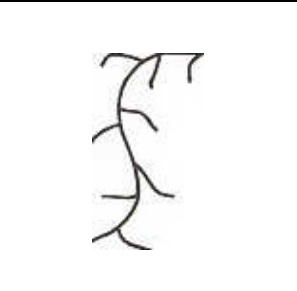
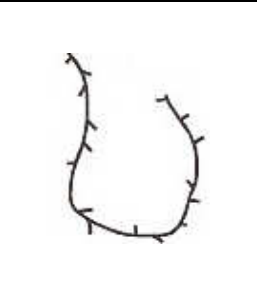
1.2.3 High density polyethylene (HDPE)

HDPE is produced by coordination or Ziegler-Natta catalysis. Its backbone is linear and contains no or few short chain branches. It is a white opaque solid that is rigid and forms films that are crispy to the touch. It is highly crystalline (70-85%). This high crystallinity increases the polymer density (0.93-0.97 g/mL) and its crystalline melting temperature (133-138°C). HDPE has higher tensile strength, stiffness and chemical resistance but it has lower permeability and resistance to stress crack than LDPE. The average molecular weight [6] of HDPE is between 200×10^3 and 500×10^3 g/mol. HDPE is resistant to many solvents and does not absorb moisture. It has a wide variety of applications such as containers (fuel tanks, laundry detergent and milk bottles), storage sheds, soft bags, pipes, folding chairs and tables, coax cable, ballistic plates, sheets and ropes.

PE with molecular weight in the millions is called ultra high-molecular weight polyethylene (UHMWPE). UHMWPE has higher tensile strength, elongation and low temperature impact resistance than HDPE.

Table 1.1 summarized the different types of commercial polyethylene [7, 8] and Figure 1.2 shows the crystal structure of polyethylene according to Bensason et al. [9].

Table 1.1: Summary of commercial polyethylene [7, 8]

PE type	LDPE	LLDPE	HDPE
Molecular structure (schematic)			
Preparation	Radical polymerization	Ziegler-Natta copolymerization	Ziegler-Natta polymerization
Degree of branching per 1,000 C-atoms	high, 20-30 long and chain branches	middle, 10-20 short chain branches up to 6 C-atoms	low, 1-3 short chain branches from 1-2 C-atoms
Degree of crystallinity (%)	45 - 65	50 - 70	70 - 85
Melting point (°C)	105 – 115	115 - 125	130 - 140
Density (g/cm ³)	0.91 - 0.93	0.92 - 0.94	0.93 - 0.97
Strength	low	medium	high
Tensile modulus (MPa)	180 - 280	270 - 530	600 - 1300
Elongation, toughness	high	medium, locally very high	low
Hardness (ShoreD)	41 - 46	50 - 60	60 - 70
Appearance	transparent	transparent	translucent
Dissolving temperature ^a (°C)	> 50	> 60	> 80

Low Density Polyethylene (LDPE), Linear Low Density Polyethylene (LLDPE), High Density Polyethylene (HDPE).

^a They dissolve in aliphatic, aromatic and halogenated hydrocarbons.

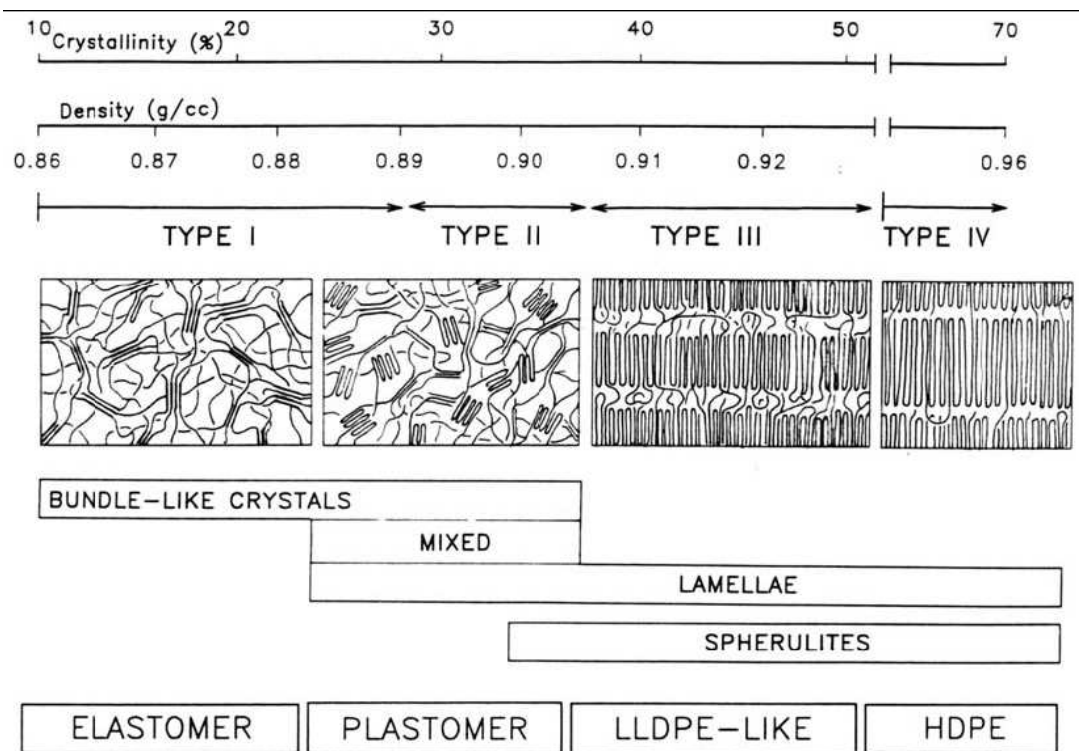


Figure 1.3 – Crystal Structure of Polyethylene according to Bensason et al. [9]

Polyolefins constitute an extremely interesting family of materials. The outstanding scientific and industrial developments of olefin polymerization processes, as well as the product properties, have led to the most aggressive, endless, always increasing, successful growth in the worldwide consumption of polyolefins [10]. This is because these thermoplastic materials are good looking, cheap, light weight and durable. The key to this huge evolution, still in progress, is the revolutionary development of the catalytic system, which can be considered as the true ‘engine’ for the innovation of this technology [11].

1.3 Types of catalyst system for olefin polymerization

Currently, the majority of polyolefin processes employ Ziegler-Natta (ZN) or chromium based heterogeneous catalysts [11-17].

1.3.1 Ziegler-Natta catalysts

In 1953, Karl Ziegler, at the University of Mülheim (Germany) discovered that highly crystalline polyethylene (HDPE) could be produced at room temperature and atmospheric pressure with heterogeneous catalyst based on titanium tetrachloride (TiCl_4) and triethylaluminum (Et_3Al) [18]. Later in 1954, Giulio Natta, at the Polytechnic Institute of Milan extended the method to other α -olefins and revealed that the Natta catalyst system (TiCl_3 - Et_3Al) affords high stereoregularity (isotacticity) polypropylene [7, 19-21]. Karl Ziegler and Giulio Natta were awarded the Nobel Prize in chemistry in 1963 for their eminent achievements. Since then, research in Ziegler-Natta catalysis for the polymerization of olefins has been widely studied and applied in academia and industry. In addition, it is today's most widely used catalyst system for the polymerization of olefins.

Conventional Ziegler-Natta catalysts are usually binary combinations of a transition metal compound of group IV –VIII and a metal alkyl of group I-III. Among the transition metals, titanium (Ti), vanadium (V) and zirconium (Zr) are particularly effective for the polymerization of olefins [7]. Of the metal alkyls of group I-III, alkylaluminums are most widely used not only because they are easily available commercially, but also because they produce highly stereoregular polymers.

The production of PE using Ziegler-Natta catalysts was first commercially available in 1955 by Farbwerke Hoechst Company. Subsequently, the industrialization of polypropylene started in 1957 at Hoechst and Montecatini. In 1963, ethylene-

propylene rubber was manufactured at Montecatini. However, the activity of the traditional Ziegler-Natta catalysts was very low and required the removal of the catalyst residue in the polymer. Therefore, the major objective was to develop a highly active catalyst which resulted in low catalyst residue in the polymer [22].

High-activity catalysts (600-1000 kg/g-Ti) were developed for ethylene polymerization in 1970 by supporting the early stage catalysts on the surface of MgCl_2 [23, 24]. In the following years (1975), Montedison and Mitsui developed high-activity (300 kg/g-Ti) and high-stereospecificity (96-99% isotactic) catalysts for propylene polymerization by means of MgCl_2 as support and electron donors [25]. In fact, these second and third generations of Ziegler-Natta catalysts solved the problems of catalyst residue removal and atactic polymer portions.

However, the major breakthrough in Ziegler-Natta catalysts (fourth generation) was made in 1980. When Kaminsky and coworkers discovered a highly active single site catalyst system made from the combination of metallocene complex (Cp_2ZrMe_2) with methylaluminoxane (MAO). This new catalyst system exhibits salient features such as high activity and homogeneity of the polymerization system, therefore, the control of the polymerization reaction. However, metallocene catalyst system requires a metal-aluminum ratio of 1 : (1000-15000) while the conventional Z-N catalyst system needs only 1 : (50-200).

Compared with other polymerization processes, Ziegler-Natta polymerization has the following features:

- The active center is composed of a transition metal-carbon bond
- High molecular weight polyethylene is formed under moderate conditions

- High molecular weight polymers can be obtained from α -olefins which may be impossible otherwise
- Various stereoregular polymers are produced
- Polymerization can be diversely controlled by choice of cocatalysts and ligands.
- They polymerize not only olefins, but also a variety of monomers such as butadiene, cycloolefins and acetylenes.

Nowadays, given the advantages of all these features, the Ziegler-Natta catalyst system is considered to be the major industrial method to initiate polymerization. In addition, it is believed that it could not be challenged by any other catalyst systems because of its versatility [26].

1.3.2 Chromium based catalysts

Chromium salts such as chromium(II) chloride (CrCl_2), chromium(III) chloride CrCl_3 and chromium(III) acetate $\text{Cr}(\text{acac})_3$ have very low activity as catalysts for olefins polymerization and therefore have never gained industrial attention [27-29].

Today, approximately 60% of the world production of high density polyethylene (HDPE) is made using the best known commercial chromium based catalysts called Phillips catalyst. This catalyst system was discovered in early 1950s and has been used by Phillips Petroleum Corporation since 1961. It is made by impregnating chromium oxide (CrO_3) on high surface silica or silica-alumina support [27]. It is currently an important catalyst in the petrochemical industry for the production of polyethylene. However, from the perspective of chemistry, not only the structure of its active site remains a mystery but also the factors which control molecular weight, molecular weight distribution and copolymerization have not been established.

Other accepted chromium based catalysts for ethylene polymerization are chromocene [30] and bis(triphenylsilyl)chromate-SiO₂-Al alkyl [31] supported on silica.

Very recently (1978), Alfred Columberg of Battelle Memorial Institute reported a new high activity catalyst system for ethylene polymerization. This catalyst, made by a modified chromium acetate [Cr(CH₃CO₂)₃] in combination with diethylaluminum chloride (AlEt₂Cl) could polymerized ethylene [32] in the temperature range of 20-230 °C with activity of 39 kg-PE/g-Cr/hr. However, no information was given on the mechanism of the reaction and the structure of the modified chromium acetate complex.

Later, Gan et al. demonstrated that the same catalyst could be obtained with a different starting material (CrCl₃.6H₂O and acetic acid) and could also be used in the homopolymerization and random copolymerization of ethylene and propylene [33, 34].

Furthermore, many modified forms of the Battelle catalysts have been reported. Soga et al. developed a soluble [Cr(C₁₇H₃₅CO₂)₃ / AlEt₂Cl] catalyst system which showed some activity for ethylene polymerization and ethylene-propylene copolymerization but not for propylene polymerization [35]. In addition, Young et al. demonstrated that [Cr(acac)₃/MgCl₂-DEAC-EB] could synthesize ethylene-propylene random copolymers with isotactic propylene sequence [36].

Since precise polymerization is being increasingly required for the detailed structural control of polymers, catalyst chemists still have an immense amount of work to do. Therefore, developing new characteristic catalyst systems and throwing light on their structure, active site, mechanism and kinetics still remain a challenge.

1.3.3 The effects of pressure

Pressure is known to affect the crystallization and physical properties of polymers. The density of the polymer is dependent on pressure much more than is the case for metals and ceramics production. Workers such as Pae and Bhateja [37, 38] have extensively reviewed the effect of hydrostatic pressure on the mechanical behavior, compressibility, crystallization and melting of polyethylene. It has also been reported that morphology and other properties of polymer melts such as melt viscosity and thermal conductivity are influenced by pressure [39].

1.4 Mechanisms of Ziegler-Natta polymerization

The mechanism of Ziegler-Natta catalysts is poorly understood because it takes place on the surface of an insoluble particle, a difficult situation to probe experimentally. Several sets of molecular descriptions have been proposed [40-42] for this polymerization reaction, but they all differ fundamentally from one another. The source of this disagreement is the very mode of carbon-carbon bond formation [43].

Today, two of the most clearly defined proposals among the many sets suggested are the carbene-to-metallacycle mechanism of Green and Rooney [42] and the direct four-center olefin insertion mechanism of Cossee and Arlman [44-46]. They are both characterized by the active site being on a monometallic or bimetallic structure. However, the mono and bimetallic nomenclatures are difficult to use for certain mechanistic proposals [27]. Consider for example, three types of active centers that have been proposed for active metal-carbon bond as represented in Figure 1.3. A common feature of growth in all these structures is the complexing of olefin to the transition metal (T_M) center. It is assumed that in structure (a) and (b), growth takes place in between the transition metal (T_M) and the growing polymer (P_n) bonds, while in

structure (c), the aluminum (Al) - growing polymer (P_n) is the growth bond. Therefore, it is not clear if the mechanism via structure (b) should be classified as mono or bimetallic.

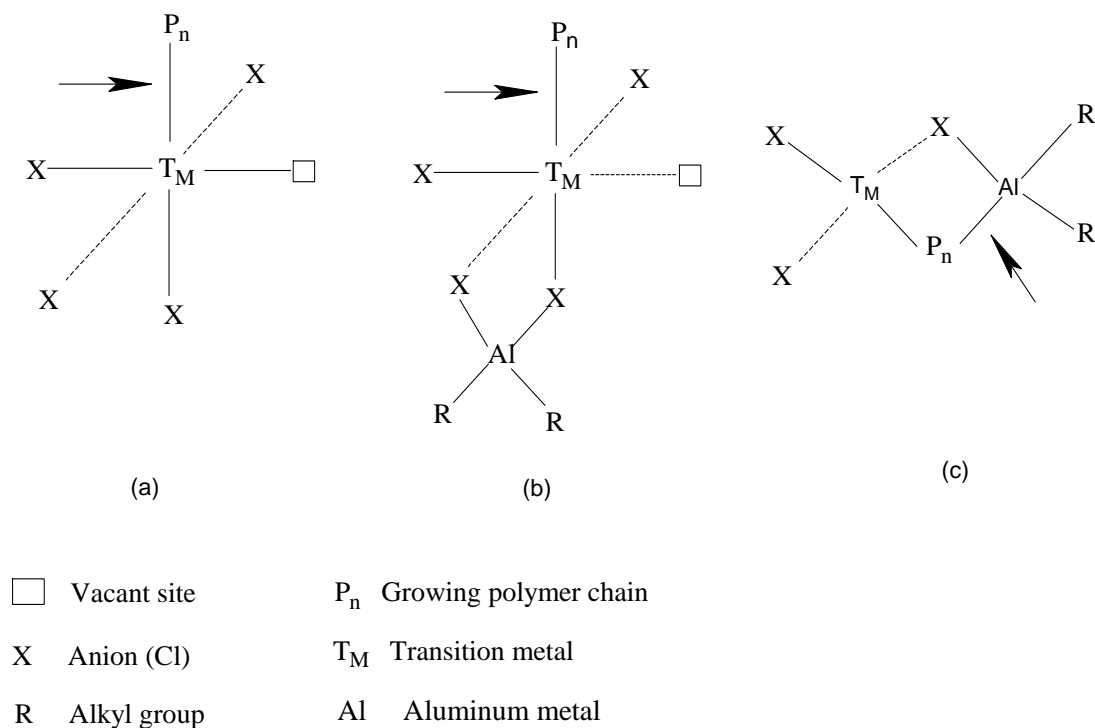


Figure 1.4: Monometallic structure versus bimetallic structure [7, 27].

According to Cossee, in the monometallic structure, the active site (transition metal) has an octahedral arrangement of four ligands, an alkyl group (growing polymer chain) and a vacant site which is essential for the initiation step. It is also assumed that the aluminum alkyl serves as an alkylating and reducing agent. The propagation reaction proceeds by coordination of an olefin to the transition metal and the subsequent insertion of the olefins in the metal-alkyl bond, which regenerates a vacant site [47]. His findings were supported by molecular orbital calculations.

Figure 1.5: represents a growth step in Cossee's mechanism of ethylene polymerization, illustrating ethylene coordination and insertion into the metal-alkyl bond.

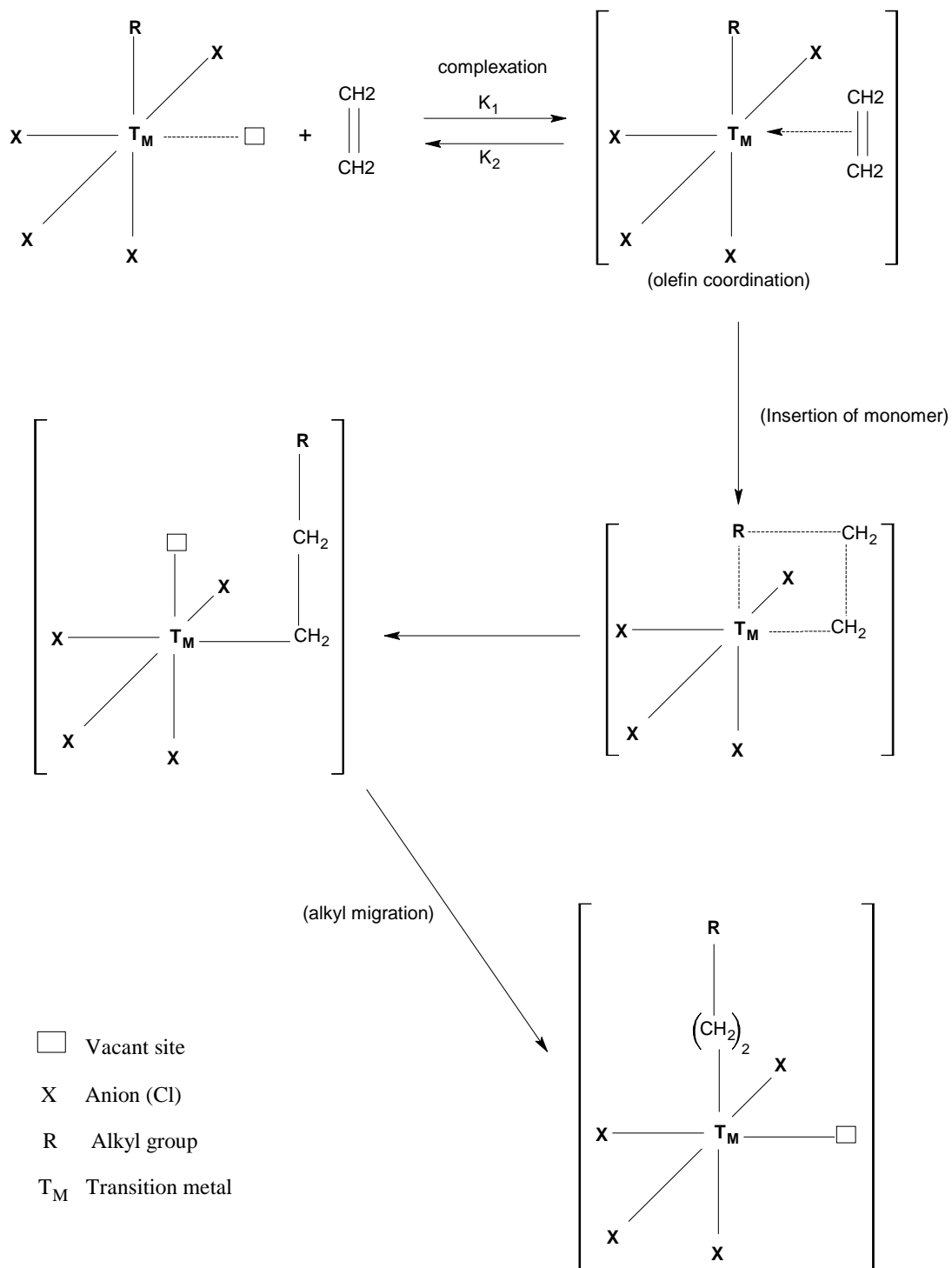


Figure 1.5: Cossee's mechanism of ethylene polymerization [47]

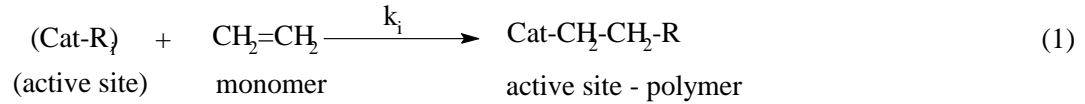
1.5 Kinetics of Ziegler-Natta polymerization

Since Ziegler's original discovery of catalysts, for low pressure polymerization of ethylene and other olefins, a number of papers have been published describing different aspects of the process and putting forward various mechanisms based on kinetic studies for the reactions involved [48-50].

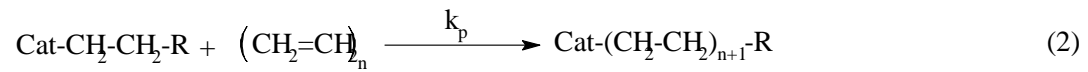
Kinetic studies are of high importance in understanding the Ziegler-Natta polymerization. This is because kinetic data help determine the rate of the polymerization, the activation energy and the nature of polymer formed with a specific catalyst system. In addition, the shapes of the rate of polymerization curve are affected by the type and surface of catalyst system, the medium used (solvent), the reaction temperature, aging time, and the ratio of metal alkyl and transition metal salt [27, 51-56].

Kinetics of ethylene polymerization using Ziegler-Natta titanium based complexes are the most widely studied Ziegler-Natta catalyst system [57-60]. A general kinetic picture of Ziegler-Natta polymerization has yet to emerge. However, most previous investigators agree that the Ziegler-Natta polymerization processes occur in these three following steps (Figure 1.6):

1. Initiation



2. Propagation



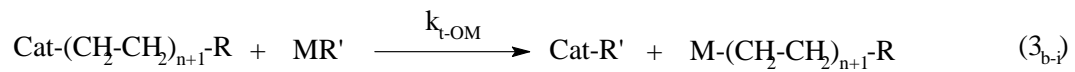
3. Chain termination

a. Spontaneous disproportionation

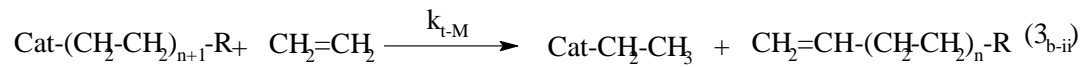


b. Chain transfer

→ Transfer with an organometallic compound (MR')



→ Transfer with monomer



c. Inactivation of active center



Figure 1.6: Kinetic scheme for Ziegler-Natta polymerization

- a. The initiation step is fast and is usually instantaneous. It occurs at the beginning of the polymerization process. In addition it is assumed that in this initiation reaction, all active centers have similar characteristics and one can use the single symbol $(\text{Cat-R})_i$ (active site i) but during the course of the polymerization process different chain transfer reactions occur and new initiation sites appear in the system with characteristics which may differ from those of $(\text{Cat-R})_i$ (initial active site i) [61].
- b. The chain propagation reaction is the addition of a monomer molecule to the propagation of the center active site-Polymer. In other words, it is assumed that in this stage, the metal-alkyl complex continues to lengthen the alkyl chain by the repeated binding and insertion of the monomer into the growing chain [62].
- c. Also referred to as the deactivation step, chain termination reactions are believed to be first order with respect of the concentration of the active centers [26].

According to Natta and coworker [63], the rate (R_p) of Ziegler-Natta polymerization is related to the concentration of the monomer and active center by the expression:

$$R_p = k_p[M]C^*$$

Where R_p is the rate of the polymerization, k_p is the propagation rate constant, $[M]$ is the monomer concentration and C^* is the active center at time t .

Since most Ziegler-Natta catalysts are heterogeneous and unstable, their activity in olefin polymerization decreases either from the beginning of the polymerization process or after the acceleration period. Thus the mechanism of the reaction is affected [64, 65]. Burfield et al. [66-68], while studying the kinetic of the polymerization of 4-

methylpentene-1 by the $\text{VCl}_3 / \text{AlR}_3$ catalyst system concluded that propagation occurred at an active center formed by the interaction of metal alkyl with the transition metal halide instead of aluminum alkyl adsorbed onto the surface of VCl_3 as had been predicted. Thus, the rate of the polymerization becomes:

$$R_p = k_p \theta_M C^*$$

Where R_p is the rate of the polymerization, k_p is the propagation rate constant with respect to the adsorbed monomer, θ_M is the fraction of the surface sites covered by adsorbed monomer and C^* is the concentration of the active site. In addition, according to the Langmuir-Hinshelwood isotherms, describing the adsorption of monomer and metal alkyl onto the catalyst surface, the fraction of the surface sites covered by adsorbed monomer (θ_M) and θ_A (for metal alkyl) expressions are:

$$\theta_M = \frac{K_M[M]}{1 + K_M[M] + K_A[A]}$$

$$\theta_A = \frac{K_A[A]}{1 + K_M[M] + K_A[A]}$$

Where $[M]$ and $[A]$ are respectively the concentration of monomer and metal alkyl; K_M and K_A are the equilibrium constants of the respective adsorption equilibrium.

Therefore the rate of the polymerization (R_p) becomes:

$$R_p = \frac{k_p C^* K_M[M]}{1 + K_M[M] + K_A[A]}$$

1.6 Trinuclear oxo-centered metal carboxylate complexes

Oxo- bridged, trinuclear metal carboxylate assemblies of the composition $[M_3O(RCOO)_6L_3]^+$ where M is a trivalent 3d-metal, L is a monodentate ligand (water, pyridine diethyl amine etc...) and R is an alkyl or substituted alkyl have been known for over a century [69] since Weinland [70] prepared the first trinuclear basic acetate complex using chromium(III) and iron(III). However, their true structures were established only in 1969 after X-ray crystallography became more widely available through better, smaller and faster computers [71, 72]. The most notable features of these complexes are that, the three metal atoms of the complex form an equilateral triangle with a trigonally coordinated oxygen atom at the center of the triangle, two carboxylate groups bridge each pair of metal and a monodentate ligand is coordinated to each metal atom, giving an octahedral configuration to the structure [73]. A 2D structure of this family of complexes is shown in Figure 1.6.

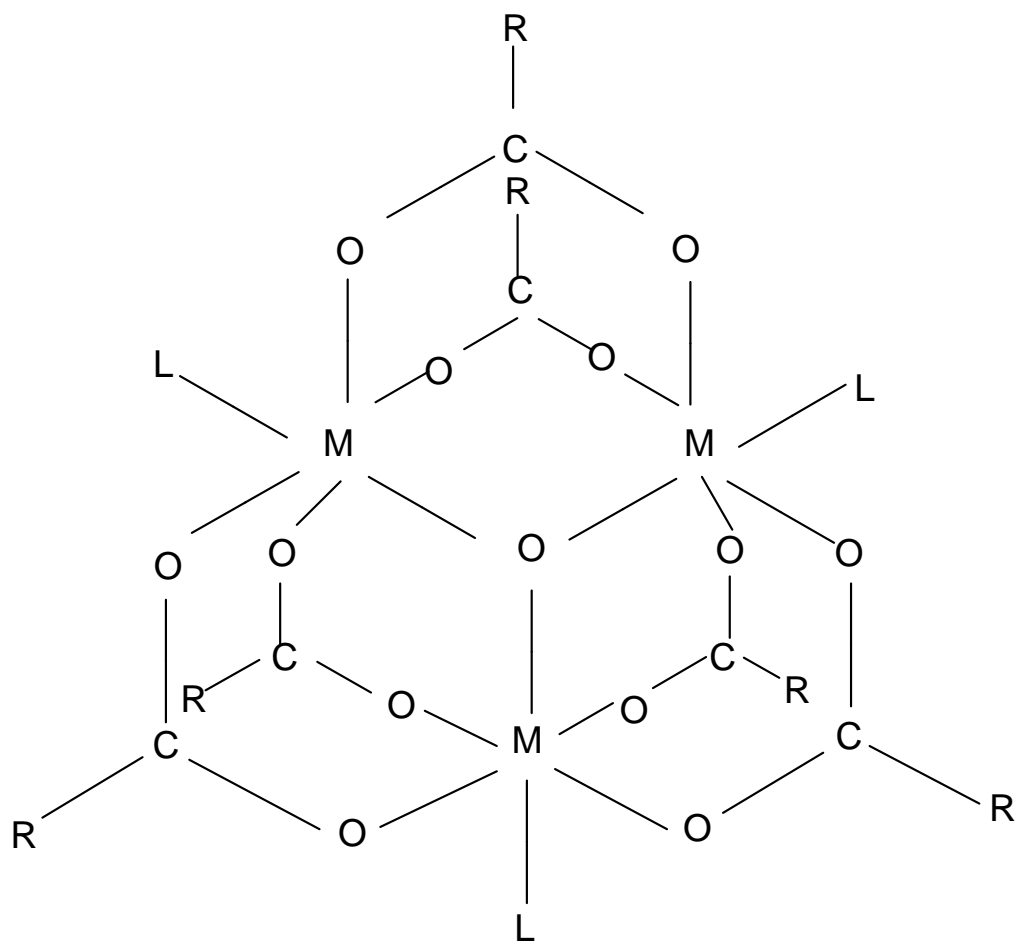


Figure 1.7: General structure of trinuclear oxo-centered carboxylate complex: $[M_3O(RCOO)_6L_3]^+$, M = metal, L = monodentate ligand and R = alkyl or aryl group.

The first X-ray structure of trinuclear oxo-centered complex reported in literature was the structure of $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl \cdot 6H_2O$ [71,72]. Since then, many X-ray diffraction studies have confirmed this general structure in the cases of iron (Fe) [69], manganese (Mn) [74,75], cobalt (Co) [76], rhodium (Rh) [75], ruthenium (Ru) [77,78], titanium (Ti) [79], vanadium (V) [80], and iridium (Ir) [75]. A review of all these complexes, $[M_3O(RCOO)_6L_3]^+$ reaches to these conclusions:

- Generally, the metal atoms of this type of structure are of same valence (M^{III}), hence all acetates are nearly isostructural. However, mixed-valence metal complexes have also been reported in literature [75].
- They differ in the type of carboxylates, monodentate ligand (L) and nature of solvates included in the crystals
- No matter what type of metal, ligand and alkyl or alkyl group used, the structure of their $[M_3O]^{6+}$ core is invariant.
- In the infrared spectra of this family of complexes, the monodentate ligands (L) are expected to exhibit metal-ligand (M-L) rocking, wagging and stretching modes beside the normal fundamental modes associated with the free ligand.

Water was known as the only monodentate ligand (L) until Cotton et al [77], reported the structure of $[Ru_3O(CH_3CO_2)_6 \cdot 3(PPh_3)]$ in 1972. Since then, the types of ligand able to coordinate the metal atoms are legion [77, 81-82]. The most frequently synthesized trinuclear oxo-centered complexes are those of basic acetate. However, a wide range of substituted carboxylate ligands such as methanoate, ethanoate, trifluoroethanoate [69], formate [76], difluoroacetate [83], carboxylatoborane [84], benzoate [85], palmitate, stearate [86] and glycinate [87, 88] have been reported in literature. Furthermore, mixed metal trinuclear oxo-centered carboxylate complexes have also been reported. However, only a few have been fully studied in detail [88].

Trinuclear (μ -oxo)-centered carboxylate complexes are of considerable current interest because of their very useful biological, physical and chemical properties [80, 89-92]. For example, heterotrinuclear clusters of Ru_2M (M = first row transition metal) have an extensive reversible redox chemistry [93] and, therefore, mixed-valence chemistry, making them potential redox catalysts [94, 95]. Moreover, some trinuclear oxo-centered complexes are used for cleaving DNA, which mimic restriction enzymes

[96]. Among all μ_3 -oxo carboxylate-bridged clusters, chromium compounds have been the most widely studied spectroscopically [76, 97], thermally [69, 98, 99], and magnetically [74,100-101]. For example, Sun et al. [102] reported in recent literature (1999) that trinuclear chromium(III) complexes may exert some control over cholesterol and triglycerides in rats. In addition, they may be used in treatment for type 2 diabetes and hyperlipidemia. This was confirmed later by Ryan et al (2003) [103]. Moreover, they are also known to stabilize the collagen molecule against enzymatic degradation [104,105]. Furthermore, trinuclear, oxo-centered carboxylate complexes of chromium have been used as precursors for the preparation of mixed-ligand ternary or quaternary complexes [106-108]. Subsequently, numerous articles appeared with oxo-centered trinuclear complexes. Some were reported to be able to polymerize olefins [26,109-111], catalyze the hydrogenation of olefins [81] and the epoxidation of olefins by molecular oxygen [112].

The synthesis and structural characterization of trinuclear oxo-centered complexes are widely investigated for academic purposes. There were only three different routes [113] known for the preparation of these complexes: the oxidation of metal(II) carboxylate with the experiment carried out under inert atmosphere [83,114-115], the reduction of chromium trioxide in acid medium [75] and the reaction of freshly precipitated chromium(III) hydroxide with slight excess of carboxylic acid [76]. However, very recently, Gan et al. [26,109-111] reported a new and simple method for the synthesis of trinuclear oxo-centered chromium(III) complexes. This novel route, which is a modification of previous methods, not only yields a high amount of product but it seems comparatively economical. Hence, this last method was used to synthesize two oxo-centered, trinuclear chromium(III) carboxylate clusters. Then, their properties as catalysts at variable pressures in Ziegler-Natta ethylene polymerization were also investigated.

1.7 Scope of this study

In spite of the simple structure of ethylene, the field of polyethylene production is a complex area with a very wide range of resin types and many different manufacturing processes. From a comparatively late start (in the 60's), polyethylene production has increased rapidly to make polyethylene the major tonnage plastic material in the world [116-118]. In the laboratory of polymer technology, the synthesis of new complexes, able to polymerize olefins with high activities and good polymer properties has always been of great interest. This is because catalyst system can affect the polymerization behavior and the polymer properties by influencing molecular weight, density, cross-linking, morphology, crystallinity and branching. It is generally known that the majority of Ziegler-Natta catalysts are unstable when exposed to air and moisture, thus the overall efficiency, when it comes to catalyst choice for industry, is determined not only by the properties of the polymer it produces, the activity of the system and the cost but also its stability and ease of handling in air.

The aim of this research was to synthesize two trinuclear (μ -oxo)-centered carboxylate complexes, stable in ambient atmosphere using Gan et al. method [26,109-111], to analyze these complexes and to test their activities in Ziegler-Natta ethylene polymerization at constant temperature and variable monomer pressures.

The synthesis of two trinuclear oxo-centered carboxylate clusters is described in chapter II. Their analyses were carried out by titration, elemental analyses, Thermogravimetry Analyses (TGA), Fourier Transform Infrared Spectroscopy (FTIR), magnetic susceptibility measurements and single crystal X-ray structure determination. These are consistent with the formulae $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCO}_2)_6 \cdot 2\text{H}_2\text{O}]\text{Cl}_3\text{CCO}_2 \cdot 3\text{H}_2\text{O}$ and $[\text{Cr}_3\text{O}(\text{F}_3\text{CCO}_2)_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$.

Chapter III details the experimental design for the polymerization reaction and the techniques used to characterize the produced polymer.

Chapter IV and V describe in details the polymerization of ethylene using $[\text{Cr}_3\text{O}(\text{F}_3\text{CCO}_2)_6 \cdot 3\text{H}_2\text{O}]\text{NO}_3 \cdot \text{H}_2\text{O}$ and $[\text{Cr}_3\text{O}(\text{Cl}_3\text{CCO}_2)_6 \cdot 2\text{H}_2\text{O}]\text{Cl}_3\text{CCO}_2 \cdot 3\text{H}_2\text{O}$ respectively in combination of AlEt_2Cl as cocatalyst. The effect of different monomer pressures and Al/Cr ratio on the crystallinity, catalyst activity and polymer yield are also reported. The resulting polymers were characterized by FTIR, DSC, TGA, NMR, DMA, density and hardness test.

The last chapter of this thesis (chapter VI) summarizes these results and describes possible future avenues for research.

1.8 References

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