CHAPTER ONE

Introduction

1.1 TRINUCLEAR OXO-CENTRED COMPLEX

Transition metal carboxylate complex can be divided into three main groups namely the dinuclear (*paddlewheel*), the trinuclear (*basic carboxylate*) and the tetranuclear (*butterfly*) complexes (Vlachos *et al.*, 2004). The *basic carboxylate* was obtained from trinuclear metal bonded to the oxygen atom to form a trinuclear oxo-centred. According to Cotton (1999), the loss of a second proton from coordinated water can lead to the formation of several types of oxo-compound where one of them is the oxygen-centred triangles which form a trinuclear oxo-centred complex.

In 1908, Weinland and Werner proposed the trinuclear formulation that introduced to the study of tri-oxo-nuclear. Further research found that the trinuclear formulation can be explained with the μ_3-O triangular geometry (Yazdanbakhsh, *et al.*, 2010). After the first complex was obtained, the chemistry of transition metal carboxylates had awakened the interest of some researchers although the study was only carried out based on the elucidation of the structures. In 1965, Figgis and Robertson managed to break the deadlock by the determining of the structure of chromium(III) carboxylate via single crystal X-ray diffraction (Fernandes, *et al.*, 1996).

Figure 1.1 shows the structure of trinuclear oxo-centred with the general formula of $[M_3O(O_2CR)_6L_3]^+$ where M represents the metal nuclei of the complexes (Cr, V, Mn, Fe, Co, Rh, Ir, Ru, W, Mo and Pd). Meanwhile, R is an alkyl or aryl group, while L is a terminal ligand (H_2O, methanol, or pyridine). The complex contains an oxo-centred triangular array of metal ions, with pairs of metal ions bridged by carboxylate ligands. Three terminal ligands were bonded to each metal ion to form an octahedral coordination (Anson C. E. *et al.*, 1997; Figuerola *et al.*, 2007; Kaczorowska & Cooper, 2010)

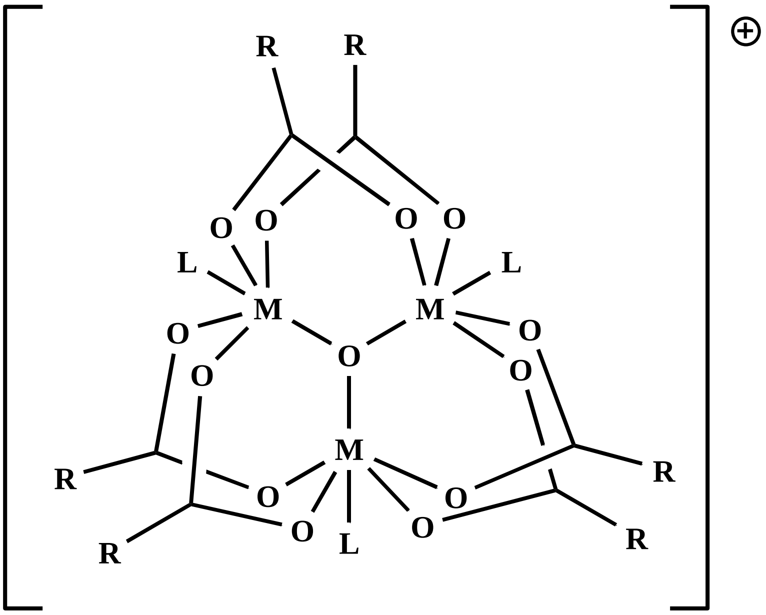


Figure 1.1: The structure of the cluster $[M_3O(O_2CR)_6L_3]^+$

Trinuclear oxo-centred carboxylate has attracted interest for further study by some researchers as the compound exhibits unique structural features. The application of the complex in electronic and magnetic study has been reported. Furthermore, the complex shows interesting properties as homogenous catalysts in various oxidation reactions that are used for experimental modelling of biocatalysts (Losada, *et al.*, 1997; Yazdanbakhsh, *et al.*, 2010).

1.1.1 Trichromium oxo-centred Complex

Generally the chromium(III) complexes tend to exist as hexacoordinated complexes (Schatschneider & Perumareddi, 2005). In 1965, Figgis and Robertson confirmed the structure of chromium(III) complex by X-ray crystallography as a trinuclear oxo-centred with carboxylate-bridge. In form of *basic carboxylate*, the general formula of the complex is $[Cr_3O(OOCR)_6(L)_3]^+$. The complex contains three Cr atoms connected to an O atom at the centre forming a triangular array. The Cr atoms are connected to each other by two bridging CH_3COO groups. The complex forms a distorted octahedral coordination with a ligand molecule L (H_2O, pyridine) coordinated to each Cr (Cotton, 1999).

Some chromium(III) complexes are active as homogeneous catalysts for a variety of oxidation reactions. Some literature reported that the complexes can act as catalysts for the polymerization of ethylene and propylene (Gan, *et al.*, 2000; Gan, *et al.*, 1985; Gan, et al., 1987a; Gan, *et al.*, 1987b). Besides, $[Cr_3O(O_2CCH_3)_6(H_2O)_3](NO_3)$ was also reported to have exciting biological properties in form of low-molecular-weight chromium-binding substance (LMWCr). The complex was used in nutritional supplements and therapeutics for adult-onset diabetes as the complex activates the kinase activity of insulin receptor in the presence of insulin (Kralovec *et al.*, 2009; Speetjens *et al.*, 1999; Yazdanbakhsh *et al.*, 2009).

1.1.2 Triiron oxo-centred Complex

Triiron oxo-centred was first synthesized and successfully characterized in detail in 1944. The complex is recognized to have three iron atoms connected to an oxygen atom at the centre with the formula $[Fe_3O(O_2CCH_3)_6(H_2O)_3].2H_2O$. The Cr atoms were connected by two bridging acetate groups. The oxo-bridged polyiron centres can also be found widespread in mineralogy and biological worlds (Rafizadeh *et al.*, 2006).

The triiron oxo-centred complex has found applications in oxidation of cyclohexane where the iron clusters acts as catalysts. The complex have also been used as model compounds for water oxidation centres in chains of electron transport in photosynthesis processes, or in proteins, whereby in both cases, two or more iron atoms were joined by µ-oxo bridges, as in hemerythrin and ferritin. The complex with formula $[Fe_2^{III}Fe^{II}O(OOCH_3)_6,L_3]$ was used to study the electronic transfer and the factors that interfere in the process (Dziobkowski *et al.*, 1981; Fernandes, *et al.*, 1996; Nakamoto *et al.*, 1997).

1.2 CHROMIUM-BASED CATALYSTS FOR POLYMERIZATION OF OLEFINS

Chromium salts such as chromium(II) chloride, chromium(III) chloride and chromium(III) acethylacetonate have long been investigated as catalysts in the polymerization of ethylene and propylene. However, their activities were relatively low compared to other Ziegler-Natta catalysts and have not gained much attention in the commercial sectors (Gan, *et al.*, 2000).

Generally, Ziegler-Natta catalysts were formed by reacting a metal alkyl (or hydride) with transition-metal salt. Many transition-metal salts in combination with certain metal alkyl (or hydride) showed some activity in the polymerization of ethylene or propylene but only those of Ti and V have been widely used in industrial. Cr salts such as $CrCl_2$, $CrCl_3$ and $Cr(acac)_3$ have also been used but their activities were generally low.

Phillips catalysts are basically made from chromium oxides supported on amorphous silica (Cr/SiO_2). The catalysts are used to produce more than 50 different types of HDPE and LLDPE without using any activator (Kukalyekar, 2007; Weckhuysen & Schoonheydt, 1999). The various modifications of the Phillips catalyst and a number of other chromium-based catalysts such as the bis(triphenylsilyl)chromate, $Cp^*Cr(THF)_2CH_3]^+BPh_4^-$ (THF is tetrahydrofuran) and neutral $Cp^*Cr[CH_2Si(CH_3)_3]_2$ where Cp* is pentamethylcyclopentadienyl (Me_5Cp) were reported to be employed in the polymerization of olefins (Gan, *et al.*, 1987; Theopold, 1998; Theopold *et al.*, 1992).

Battle has discovered a new Ziegler-Natta catalysts system derived from chemical modification of chromium acetate with a mixture of acetic anhydride and acetic acid. With combination of $AlEt_2Cl$, the polymerization of ethylene and/or propylene by using $Cr(CH_3COO)_3.H_2O$ was reported to show the highest activity. Soga *et al.* have developed a soluble chromium catalytic system comprising of $Cr(C_{17}H_{35}COO)_3$ and $AlEt_2Cl$, that can be used in the homo- and copolymerization of ethylene and propylene (Gan *et al.*, 2000; Gan *et al.*, 1987; Soga *et al.*, 1985a, 1985b)

1.3 ZIEGLER-NATTA POLYMERIZATION

Sequence of research by Ostwald in 1909 on catalytic action, Sabatier in 1912 on the hydrogenation of organic compounds by metal powder and Haber in 1918 on ammonia synthesis have led to the development of the science of catalysis. These three scholars have been awarded Nobel Prize as K. Ziegler and G. Natta for their work. The discovery of Ziegler-Natta catalyst highly influenced the development of basic and applied catalysis (Boening, 1966; Keii, 1972).

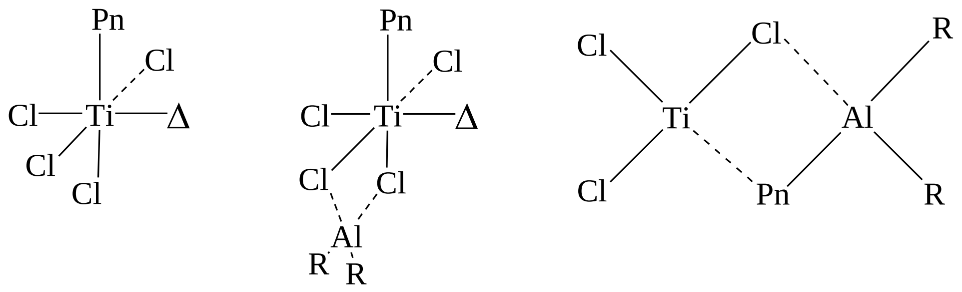
The history of Ziegler-Natta catalysts for polymerization started when K. Ziegler and G. Natta discovered the secret of the polymerization especially for high density polyethylene (HDPE) (Boor, 1979; Keii, 1972). In 1953, Karl Ziegler had synthesized HDPE using combination of a transition metal compound and an aluminium alkyl via ‘Aufbaureaktion’ reaction. While in 1954, Giulio Natta and his co-workers were successful in polymerization of propene to obtain a tacky solid using the Ziegler catalyst at Milan Polytechnic (Kukalyekar, 2007).

Ziegler-Natta catalysts were developed from a combination between two different groups of metal compounds. Compound based on a transition metal salt of metal group IV to VII acting as catalysts and a metal alkyl of based metal alkyls of group I to III as a cocatalyst. Even though many studies concerning the combinations of metal alkyls and transition metals were carried out, not all combinations could be used in practice. Generally, the transition metal compounds containing Ti, V and Cr and the aluminium alkyls such as $AlEt_3$, $Al\text{-}i\text{-}Bu_3$ and $AlEt_2Cl$ are used as co-catalysts (Boor, 1979; Keii, 1972; Kim & Somorjai, 2001; Kukalyekar, 2007; Soares, Kim *et al.*, 1997).

The Ziegler-Natta catalyst contains the organometallic complex as a catalytic material that possesses stereospesific catalysis and forms new types of polymers such as stereoregular polymers. These catalysts are used worldwide to produce high density (linear) polyethylene and isotactic polypropylene that lead to huge impact in the world of plastics industry. (Boor, 1979; Keii, 1972; Kukalyekar, 2007; Soares, *et al.*, 1997).

1.4 MECHANISMS OF ZIEGLER-NATTA POLYMERIZATION

There are four types of growth centre that can be used to explain the mechanism of the Ziegler-Natta polymerization, namely a transition metal-carbon bond, a based metal-carbon bond, a bound radical and a bound anion. However, the transition metal-carbon bond was the most agreed growth step to be used to determine the mechanism as the preponderance of experimental proof. According to Boor (1979), the growth step of transition metal-carbon bond can be described in the monometallic and bimetallic structures where one or two metal atoms are involved respectively. **Figure 1.2** shows three types of active centres that are used in describing the growth step. Structure **I** is a monometallic structure, structure **III** is a bimetallic structure while structure **II** is a mono- or bimetallic structure where Pn is the growing polymer chain. Δ is the vacant octahedral position.



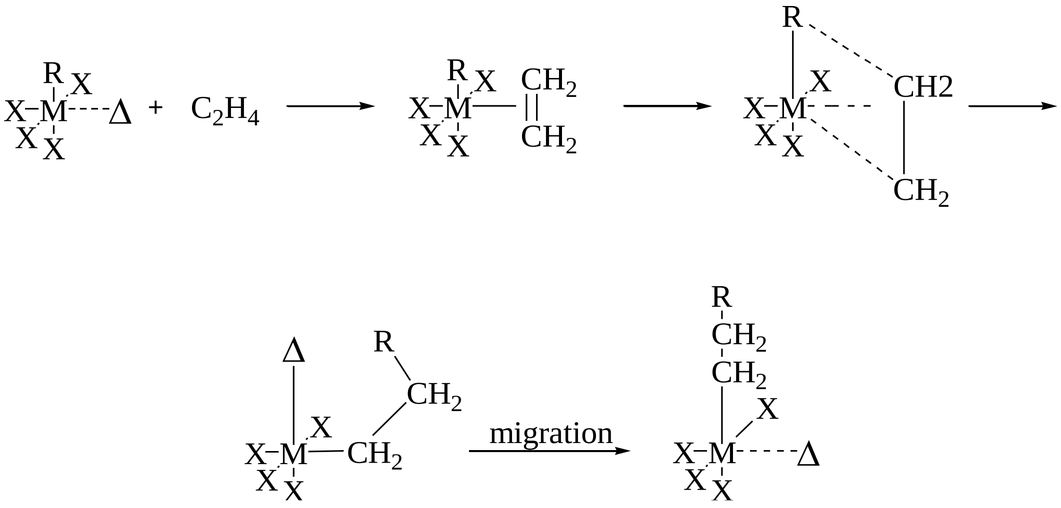
I II III

Figure 1.2: Types of active centres

1.4.1. Monometallic mechanism

Cossee (Boor, 1979) suggested the reaction mechanisms of the Ziegler-Natta catalysis based on molecular orbital calculations. In the mechanism, the active site is a transition metal atom in an octahedral configuration, where 3d orbitals of the transition metals hybridize with the π*-antibonding orbitals of olefins. One missing ligand causes a vacancy (Δ) while, the remaining positions are being occupied by one alkyl and four ligands. At least one transition metal-carbon bond or transition metal-hydrogen bond must occurr during the reaction to form one coordination place that acts as the active site of the complex (Huang & Rempel, 1995).

Scheme 1.1 shows the Cossee's mechanism where R is the growing polymer chain, X is the ligand (Cl in $TiCl_3$) and Δ is the vacant octahedral position. First step in the Cossee's mechanism is the complexation of monomer to the active site in the transition metal atom by generating a vacant coordination site. After that, the complex monomer is attached to the bond of the transition metal atom and first carbon atom of the polymer chain (R) by formal migration of the polymer chain to form a metal-carbon bond. The chain growth of polymer occurred by the repetition of the recreates a vacant coordination site at the site originally occupied by the polymer chain and the process continues. The coordination of olefin to the transition metal ion at the vacant octahedral position is through π bonding (Boor, 1979; Huang & Rempel, 1995; Keii, 1972).

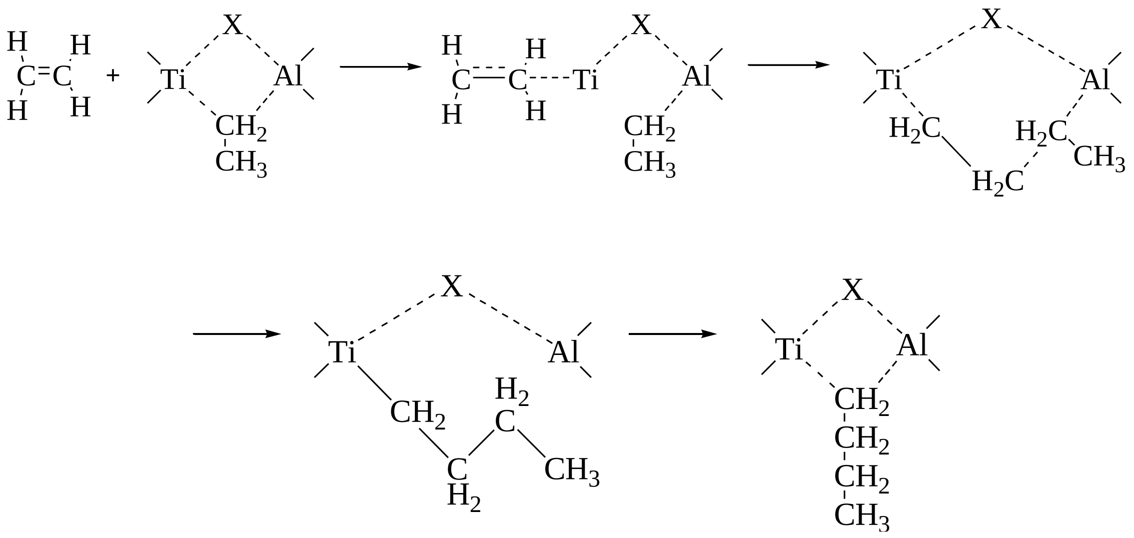


Scheme 1.1: Growth step in Cossee's mechanism (Boor, 1979)

The Cossee's mechanism was further investigated by Shogo Sakai due to the generic mechanism of olefin insertion. There are two steps of mechanism involved which is the formation of the additional complex without a barrier and the production of the insertion product (Sakai, 1991, 1994).

1.4.2. Bimetallic mechanism

In 1960, Natta proposed mechanism for polymerization of ethylene based on bimetallic mechanisms. Earlier, a related mechanism was proposed by Patat and Sinn but in a slightly different approach. Scheme 1.2 shows the opening of an Al-C formed by monomer is coordinated to the Ti atom, activates it and transfers to Al. According to Natta, the olefin is simply inserted between the existing titanium-carbon bonds through the polarization mechanism where, the Ti-polymer partial bond is broken and inserted into the Al-C bond simultaneously. An electron-deficient metal is formed as the bridged bond opens and attracts the π-electrons from the monomer into σ-type bond. In the meantime, the carbanion produced attacks the electron-deficient centre in the monomer to form a new bridged bond structure which includes the formerly complexed monomer. Patat and Sinn suggested that the olefin is partially bonded between the titanium and the methylene of the ultimate group of the polymer chain which was partially bonded to the aluminium. When the bond between the olefin and methylene forms, the titanium–carbon bridged bond is re-established to the terminal carbon, including the monomer (Allinger & Eliel, 1974; Boor, 1979; Keii, 1972).



Scheme 1.2: Bimetallic mechanism for ethylene polymerization

1.4.3. The trigger mechanism

There were some problems arose from Cossee mechanism nevertheless, Ystenes (Ystenes, 1991) managed to overcome the problems by proposing the trigger mechanism. The trigger mechanism was derived based on the interaction between two monomers where the propagation process obtained from the insertion of a complexed monomer triggers by the incoming monomer. There are three main characters for the propagation step of the mechanism; firstly, the coordination site is always occupied by a monomer. Secondly, the Lewis bases cannot attack the monomer site because the complexed monomer is only inserted when a new monomer is ready to complex. Lastly, the active metal complex is associated by two monomers though only one monomer coordination site is obtained because in the transition state, a second monomer can expand its coordination sphere transiently.

In the complexation step, stereochemical discrimination occurs when the second monomer is attached to the active complex because of the interaction between the two monomers and the other ligands of the complex. Hence, the complexation of the first monomer is harder than the complexation of the other monomer. In the trigger mechanism, the formation of the active centre in the initiation step is dependent on the concentration of monomer due to the action of a monomer unit. The mechanism proposes that the first inserted monomer is lower in stereoregularity (Huang & Rempel, 1995).

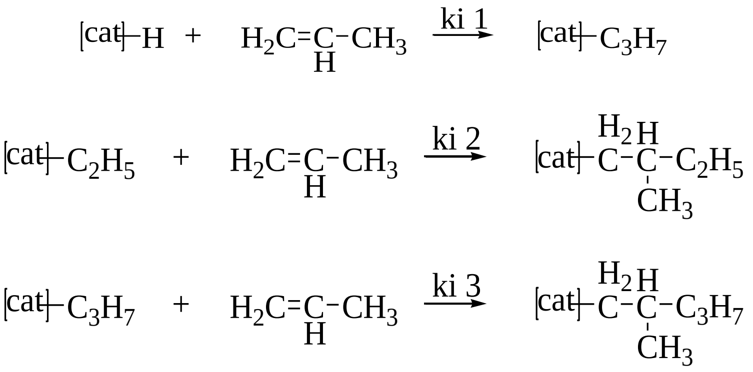
1.5 KINETICS OF ZIEGLER-NATTA POLYMERIZATION

The kinetic of the polymerization can be divided into two main types of rate curves: the decay type and the acceleration type or build-up type. The decay curve shows a build-up period in early stage where the rate of polymerization increases rapidly to a maximum and then the rate decreases gradually to the stationary state due to decay period. Whereas, acceleration curve begins with a gradual increase in the build-up period until the stationary state is reached directly. There are several factors affecting the kinetics of the polymerization such as nature of the catalysts, stirring speed, temperature and time of polymerization (Boor, 1979; Keii, 1972).

Boor suggested that some events occur in the build-up period or could also be described as the induction period. First, the formation of the active site from the reaction of the metal alkyl and transition metal. Second, the introduction of monomer gas to the active centres through the liquid phase. Third, the polymerization process is obtained and lastly, the exposure of new surface and the formation of new centres as the catalyst particle begins to break up (Boor, 1979).

Natta and co-workers described the Ziegler-Natta polymerization in three different steps starting with initiation, propagation and termination. **Scheme 1.3** presents the kinetic scheme proposed by Natta and co-workers. The notations [cat-]-R was a metal-carbon bond representing the active centre. The active metal could be a transition metal or a base metal. The [cat-]-R centre remains active in the termination reaction for further polymerization though the chains growth has stopped. Some impurities were added to react with [cat-]-polymer for inactivation of the centre in the termination of chain growth (Boor, 1979).

(i) Initiation

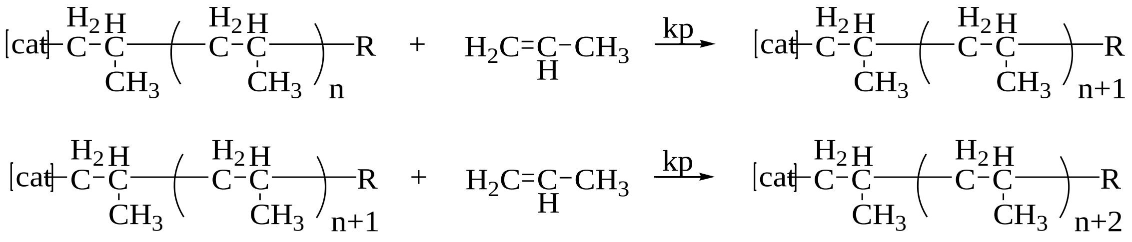


$$[cat]-H + H_2C{=}\underset{H}{C}-CH_3 \xrightarrow{ki\ 1} [cat]-C_3H_7$$

$$[cat]-C_2H_5 + H_2C{=}\underset{H}{C}-CH_3 \xrightarrow{ki\ 2} [cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-C_2H_5$$

$$[cat]-C_3H_7 + H_2C{=}\underset{H}{C}-CH_3 \xrightarrow{ki\ 3} [cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-C_3H_7$$

(ii) Propagation

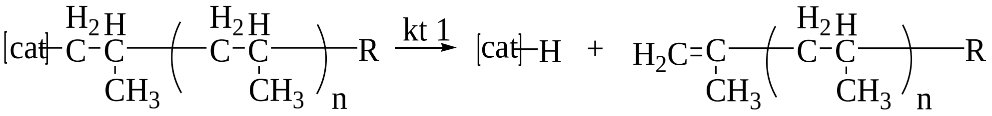


$$[cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R + H_2C{=}\underset{H}{C}-CH_3 \xrightarrow{kp} [cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_{n+1}-R$$

$$[cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_{n+1}-R + H_2C{=}\underset{H}{C}-CH_3 \xrightarrow{kp} [cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_{n+2}-R$$

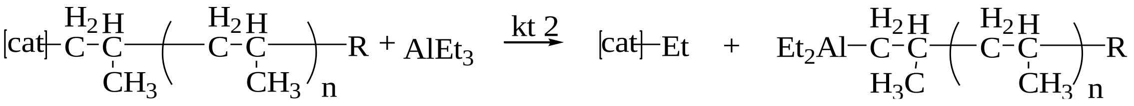
(iii) Chain termination

Disproportionation



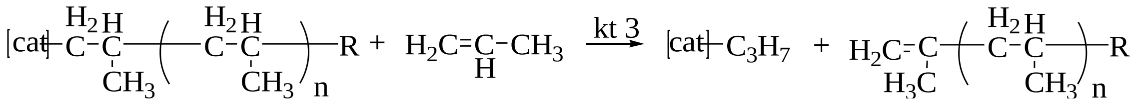
$$[cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R \xrightarrow{kt\ 1} [cat]-H + H_2C{=}\underset{CH_3}{C}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R$$

Transfer by $AlEt_3$



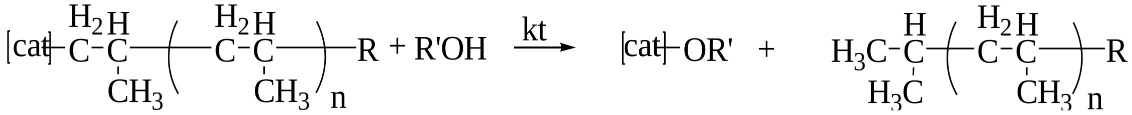
$$[cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R + AlEt_3 \xrightarrow{kt\ 2} [cat]-Et + Et_2Al-\overset{H_2}{C}-\underset{H_3C}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R$$

Transfer by monomer



$$[cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R + H_2C{=}\underset{H}{C}-CH_3 \xrightarrow{kt\ 3} [cat]-C_3H_7 + H_2C{=}\underset{H_3C}{C}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R$$

Inactivation of active centre

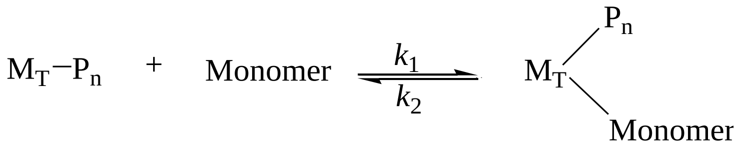


$$[cat]-\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R + R'OH \xrightarrow{kt} [cat]-OR' + H_3C-\underset{H_3C}{\overset{H}{C}}-\left(\overset{H_2}{C}-\underset{CH_3}{\overset{H}{C}}\right)_n-R$$

Scheme 1.3: Kinetic scheme proposed by Natta and coworkers (Boor, 1979)

The rate of Ziegler-Natta polymerization was proposed using a kinetic model discovered by Cossee in 1967. In this model the two step mechanism in the propagation reaction is presented below (Huang & Rempel, 1995):

i. The complexing of a monomer (M) at the transition metal-carbon centre (M_T-P_n)



(A) (M) (MA)

ii. The insertion of the monomer into the transition metal-carbon bond

(MA) (A')

Under the steady-state condition, d[MA]/dt = 0,

$$-\frac{d[M]}{dt} = \frac{k_1\, k_3\, [C]\, [M]}{k_1\, [M] + k_2 + k_3}$$

Where [C] = [MA] + [A], and [A] = all vacant sites. According to Cossee, step 2 is the rate-determining reaction and $k_2 >> k_1[M] > k_3$, so that the polymerization rate R_p is expressed as:

$$R_p = (k_1k_3 / k_2)[C][M]$$

Adsorptions kinetic played an important role to describe heterogeneous Ziegler-Natta catalysts systems (Boor, 1979; Burfield *et al.*, 1972a; Burfield & Tait, 1972; Burfield *et al.*, 1972b; McKenzie *et al.*, 1972). So, the fraction of active centre with adsorbed monomer, θ_M and the fraction with adsorbed Al cocatalyst, θ_A are expressed in terms of Langmuir-Hinselwood isotherm as:

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

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

Where K_A and K_M are the equilibrium constants for adsorption of A and M over the surface of the transition metal salt crystals respectively. Therefore, the rate of polymerization given by:

$$R_p = k_p \, \theta_A \, \theta_M$$

1.6 POLYOLEFINS

Polyolefin refers to oily or waxy texture that only contains non-aromatic carbon and hydrogen atoms. Owing to its special characters such as nonpolar, nonporous and low-energy surface have made polyolefins a commodity thermoplastic. The history of polyolefins started in 1890s with the discovery of polymethylene synthesized from diazomethane. Furthermore, in 1930s, a higher molecular weight resin from ethylene was produced at high pressure in the presence of oxygen. The discovery of HDPE by

Karl Ziegler in 1953 and the polymerization of propene in 1954 by Giulio Natta (Kukalyekar, 2007; Sailors & Hogan, 1981) expanded the interest in polyolefins.

Polyolefins are a thermoplastic type polymer that have undergone a tremendous growth and still have further growth potential as commercial polymers. Polyolefins are widely used in daily life applications due to their versatility in properties and applications, low cost and easily available raw materials. Usually, polyolefins are fabricated by extrusion, injection molding, compression molding, injection blow molding and calendaring. The various new polyolefins produced from several techniques such as homopolymers, copolymers, polymer blends and graft polymers have lead to the discovery of new polyolefins with better characateristic with accompanying economical cost performances (Boening, 1966; Zhang, 2007).

Polyolefins are the most widely used commercial polymers and these include polyethylene (PE), polypropylene (PP), poly(1-butene), poly(1-octene), poly(4-methyl-1-pentene), ethylene-propylene elastomer (EPR), and etylene-propylene-diene rubber (EPDM). Polyethylene and polypropylene are the most important and common types of polyolefins in the world. Malaysia has become the centre of polyolefins production such as polyethylene, polypropylene, polyethylene terephthalate and polyvinyl chloride. **Table 1.1** shows the polyolefins facilities in Malaysia (*Malaysia Petrochemicals Report - 2012*, 2012).

Table 1.1 : Malaysia's Polyolefins Facilities (*Malaysia Petrochemicals Report - 2012,* 2012)

Product	Company	Location	Capacity, tpa
HDPE	Titan Petchem	Pasir Gudang	120 000
LDPE	Petlin	Kerteh	255 000
LDPE	Titan Petchem	Pasir Gudang	220 000
LLDPE	Polyethylene Malaysia	Kerteh	150 000
LLDPE	Titan Petchem	Pasir Gudang	230 000
PP	Polypropylene Malaysia	Gebeng, Kuantan	80 000
PP	Titan Petchem	Pasir Gudang	200 000
PP	Titan Petchem	Pasir Gudang	280 000
PET	MPI Polyester Industries	Shah Alam	35 000
PET	Penfibre	Prai	30 000
PET	Recron Malaysia	Nilai	150 000
PVC	Industrial Resins (Malaysia)	Johor Baharu	30 000
PVC	Kaneka Paste Polymer	Gebeng, Kuantan	30 000
PVC	Malayan Electro-Chemical Industry Company	Prai	50 000
PVC	Vinyl Chloride (Malaysia)	Kerteh	150 000

1.6.1 Polyethylene (PE)

The history of PE started when British chemists, Eric Fawcett and Reginald Gibson discovered a solid form of PE in 1935. The solid that was synthesized under high-temperature, high-pressure conditions yielding a highly branched structure was named as low-density polyethylene (LDPE). In 1953, Karl Ziegler of the Kaiser Wilhelm Institute (renamed the Max Planck Institute) and Erhard Holzkamp invented high-density polyethylene (HDPE) using catalyst (Bower, 2002; Cheng, 2008; Gabrie, n.d.; Olley, 2002).

PE is a semicrystalline polymeric material which consists of two phases; crystalline and amorphous. The crystalline lamellae provide polyethylene with structural integrity, while the amorphous parts provide polyethylene with its elastic properties. The semicrystalline properties made PE to become one of the most important polymers in the world (Cheng, 2008).

PE is a simple polymer that contained basic repeating unit of ($-CH_2–CH_2-$). The structure of PE will determine the differences in properties and applications. There are three main classes of PE called high-density polyethylene, low-density polyethylene and linear low-density polyethylene. **Figure 1.3** shows the branch structure of HDPE, LLDPE and LDPE. HDPE is commonly made by the homo-polymerization of ethylene or copolymerization of ethylene with a small amount of higher α-olefins. LLDPE was produced by copolymerization of ethylene with small amount of 1-alkene at low temperature. Meanwhile, LDPE is produced from free radicals reaction at high-pressure, high temperature. LDPE contains about 20-30 branches per-thousand carbon atoms including ethyl, butyl, pentyl, hexyl and longer units (Bower, 2002; Cheng, 2008).

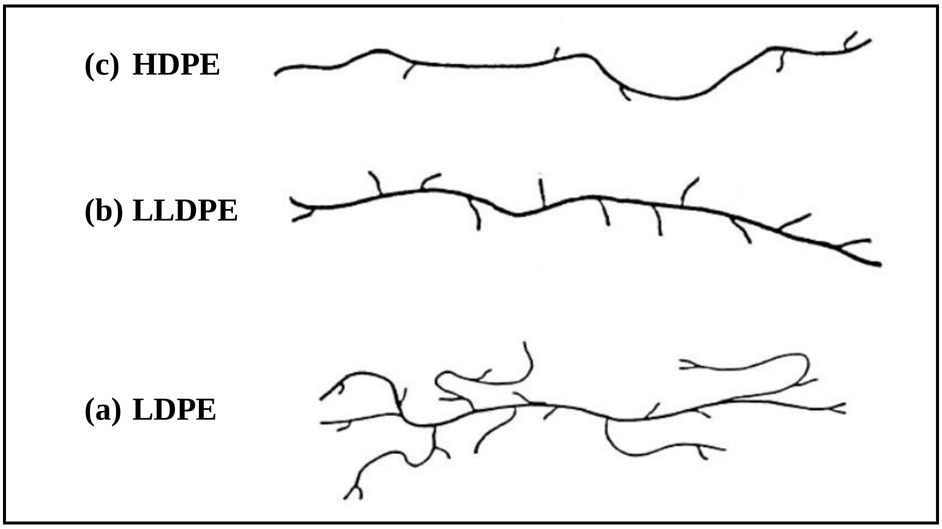


Figure 1.3: Branch structures of PE

PE occurs in several types that influence some major properties such as molecular weight (MW), molecular weight distribution (MWD), density, percentage crystallinity and degree of long chain and short chain branching. Molecular weights and molecular weight distribution are the main factors that affect processability and mechanical properties of polyethylene. Broad MWD material is easier to process due to the presence of shorter chains that act as “lubricant”. Branching in polyethylene chains affects material density and other properties such as rheological properties. There are two types of branching, short chain branching (SCB), mostly due to introduction of co-monomer, and long chain branching (LCB) formed from side reactions during polymerization. Short chain branches interfere with the formation of lamellae, and therefore affect crystallinity and density of the semicrystalline polymer.

The crystallinity and morphology of PE are closely related to the change in density. Hence, the stiffness and tensile yield strength of PE increases as the density is increased. Table 1.2 shows four categories of PE according to ASTM standards. LDPE is defined by a density range of 0.910 – 0.925 g/cm^3 because the chains do not pack into the crystal structure because of high degree of short and long chain branching. The density of LLDPE is in the range of 0.915 - 0.925 g/cm^3 as the polymer is linear, with significant numbers of short branches. MDPE is defined by a density in the range of 0.926 – 0.940 g/cm^3, whereas, the density of HDPE is in the range of 0.940 – 0.959 g/cm^3 due to the low degree of branching, strong intermolecular forces and tensile strength (Ratzlaff, 2004).

Table1.2: Classification of polyethylene by density

PE Type	Density (g/cm^3)
Low	0.910 – 0.925
Medium	0.926 – 0.940
High	0.940 – 0.959
High density homopolymer	0.96 and above

1.7 SCOPE OF STUDY

The purpose of the study was to prepare Ziegler-Natta catalysts based on Cr(III)- and Fe(III)-carboxylate in combination with diethyl aluminum chloride as co-catalyst. The catalysts will be used in the polymerization of ethylene to study the optimum molar ratio of Al/Cr and the effect of combination of Cr-Fe in the catalysts towards polymerization. Besides, the polymerizations were performed by varying the temperature to find the appropriate temperature that could produce the optimum polymer yield. Moreover, some modifications were made to the solvent system by adding natural rubber (SMRCV). The main parameters of interest to discover are the rate of catalytic activity and the characterization of polymer.

First chapter describes about the background of the study, history of Ziegler-Natta catalysts and some literature review of the topic. Chapter two describes the preparation of complexes **CI[1]**, **CI[2]**, **CI[3]**, **CI[4]** and **CI[5]**. These complexes were prepared by reaction of Cr(III) and Fe(III) salts with carboxylate acids under several condition. Some physical measurements of the complexes were carried out. Furthermore, the complexes were characterized by IR spectroscopy, UV-visible spectroscopy, CHN-elemental analysis, ICP-OES, TGA and X-ray crystallography. The characterizations of complexes are discussed in details in this chapter.

Chapter three delineates the polymerization of ethylene. The polymerization procedures are discussed from the gasline setup, the preparation of reaction flask, the polymerization process to the collecting of the polymer product. The polymers were characterized using IR spectroscopy, TGA and DSC. In this chapter, the polymerization properties such as catalytic activity and polymer yield are discussed. Several factors that affect the polymerization of ethylene were investigated such as the effect of varying Al/Cr molar ratio, the effect of mixed-metal complexes, the effect of substituent group in the catalysts and the effect of variation of temperature. The kinetic study for the polymerization of ethylene is also discussed. Lastly, the characterization of polymer is also discussed which includes the thermal properties and the percentage of crystallinity.

Chapter four illustrates the modification of the polymerization of ethylene with the natural rubber (SMRCV). Methodology of the polymerization of ethylene-SMRCV is discussed in details where the solvent system was modified. The solvent systems were prepared by adding variable amounts of SMRCV. Effect of the addition of SMRCV into solvent towards polymerization and polymers produced are deliberated clearly. The polymers formed were characterized and are discussed in terms of thermal stability and the percentage of crystallinity. Finally, Chapter five concludes the scope of study and some recommendations for future research.

References

Allinger, N. L., & Eliel, E. L. (1974). *Topics in Stereochemistry*. New Yoek: John Wileys & Sons, Inc.

Anson C. E., Bourke J. P., Cannon R. D., Jayasooriya U. A., Molinier M., & Powell, A. K. (1997). Crystal Structures of the Isomorphous Prototypic Oxo-Centered Trinuclear Complexes $[Cr_3O(OOCCH_3)_6(H_2O)_3]Cl\cdot 6H_2O$ and $[Fe_3O(OOCCH_3)6(H2O)_3]Cl\cdot 6H_2O$. *Inorganic Chemistry, 36*(6), 1265–1267.

Boening, H. V. (1966). *Polyolefins structure and properties*. Amsterdam-London-New York: Elsevier Publishing Company.

Boor, J. (1979). *Ziegler-Natta catalysts and polymerizations*. New York: Academic Press.

Bower, D. I. (2002). *An introduction to polymer physics*. United Kingdom: Cambridge University Press.

Burfield, D. R., McKenzie, I. D., & Tait, P. J. T. (1972a). Ziegler-Natta catalysis: 1. A general kinetic scheme. *Polymer, 13*(7), 302-306.

Burfield, D. R., & Tait, P. J. T. (1972). Ziegler-Natta catalysis: 3. Active centre determination. *Polymer, 13*(7), 315-320.

Burfield, D. R., Tait, P. J. T., & McKenzie, I. D. (1972b). Ziegler-Natta catalysis: 4. Quantitative verification of kinetic scheme. *Polymer*, *13*(7), 321-326.

Cheng, J. J. (2008). *Mechanical and chemical properties of high density polyethylene: Effects of microstructure on creep characteristics.* Ph.D. dissertation, University of Waterloo, Canada.

Cotton, F. A. (1999). *Advanced inorganic chemistry* (6 ed.). New York: John Wiley & Sons.

Dziobkowski, C. T., Wrobleski, J. T., & Brown, D. B. (1981). Magnetic properties and Moessbauer spectra of several iron(III)-dicarboxylic acid complexes. *Inorganic Chemistry, 20*(3), 671-678.

Fernandes, C., Stadler, E., Drago, V., Jorge da Cunha, C., & Hiroko Kuwabara, I. (1996). Mössbauer, vibrational and electronic spectroscopy of trinuclear μ-oxo iron(III) acetate clusters with pyridine and derivatives as ligands. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy, 52*(14), 1815-1821.

Figuerola, A., Tangoulis, V., Ribas, J., Hartl, H., Brüdgam, I., Maestro, M., et al. (2007). Synthesis, crystal structure, and magnetic studies of oxo-centered trinuclear chromium(III) complexes: [Cr3(μ3-O) (μ2-PhCOO)6(H2O)3]NO 3·4H2O·2CH3OH, a case of spin-frustrated system, and. *Inorganic Chemistry, 46*(26), 11017-11024.

Gabrie, L. H. (n.d.). HISTORY AND PHYSICAL CHEMISTRY OF HDPE. *Chapter One*. Retrieved from http://www.plasticpipe.org/pdf/chapter-1_history_physical_chemistry_hdpe.pdf

Gan, S. N., Aishah, M. J., & Ooi, C. P. (2000). Trinuclear oxo-centered chromium(III) carboxylate complexes as Ziegler-Natta catalysts for ethylene polymerization. In T. Sano, Uozumi, T., Nakatani, H and Terano, M. (Ed.), *Progress and Development of Catalytic Olefin Polymerization* (pp. 25-32). Tokyo: Technology and Education Publishers.

Gan, S. N., Burfield, D. R., & Soga, K. (1985). Differential scanning calorimetry studies of ethylene-propylene copolymers. *Macromolecules, 18*(12), 2684-2688.

Gan, S. N., Chen, S. I., Ohnishi, R., & Soga, K. (1987a). Homo- and copolymerization of ethylene and propylene using a heterogeneous chromium catalyst system. Polymer, vol 28, 1391-1395. *Polymer, 28*, 1391-1395.

Gan, S. N., Lim, M. C., Chen, S. I., & Soga, K. (1987b). Modified Chromium(III) Acetate Used in the Polymerization of α-Olefins. *Journal of Catalyst, 105*, 249-253.

Huang, J., & Rempel, G. L. (1995). Ziegler-Natta catalysts for olefin polymerization: Mechanistic insights from metallocene systems. *Progress in Polymer Science, 20*(3), 459-526.

Kaczorowska, M. A., & Cooper, H. J. (2010). Electron Induced Dissociation: A Mass Spectrometry Technique for the Structural Analysis of Trinuclear Oxo-Centred Carboxylate-Bridged Iron Complexes. *Journal of the American Society for Mass Spectrometry, 21*(8), 1398-1403.

Keii, T. (1972). *Kinetics of Ziegler-Natta polymerization*. Tokyo: Kodansha.

Kralovec, J. A., Potvin, M. A., Wright, J. H. D., Watson, L. V., Ewart, H. S., Curtis, J. M., Barrow C. J. (2009). Chromium(III)–docosahexaenoic acid complex: Synthesis and characterization. *Journal of Functional Foods, 1*(3), 291-297.

Kukalyekar, N. (2007). *Bimodal Polyethylenes from One Pot Synthesis; Effect of Flow Induced Crystallization on Physical Properties.* Unpublished Ph. D Theisis, Eindhoven University of Technology, Yellapur, India.

Losada, G., Mendiola, M. A., & Sevilla, M. T. (1997). Synthesis, characterization and electrochemical properties of trinuclear iron(III) complexes containing unsaturated carboxylate bridging ligands. *Inorganica Chimica Acta, 255*(1), 125-131.

Malaysia Petrochemicals Report - 2012. (2012). London, United Kingdom, London: Business Monitor International.

McKenzie, I. D., Tait, P. J. T., & Burfield, D. R. (1972). Ziegler-Natta catalysis: 2. A kinetic investigation. *Polymer, 13*(7), 307-314.

Nakamoto, T., Hanaya, M., Katada, M., Endo, K., Kitagawa, S., & Sano, H. (1997). The Valence-Detrapping Phase Transition in a Crystal of the Mixed-Valence Trinuclear Iron Cyanoacetate Complex [$Fe_3O(O_2CCH_2CN)_6(H_2O)_3$]. *Inorganic Chemistry, 36*(20), 4347-4359.

Olley, R. H. (2002). The Story of Polythene. *The World's No. 1 Plastic*. Retrieved from http://www.personal.rdg.ac.uk/~spsolley/pe.html

Rafizadeh M., Naseh M., & Amani., V. (2006). Crystal Structure of Trinuclear, Oxo-cenetered Base Carboxylate, Fe(III) Complex Cointaining DMSO Ligand and Anion of Fe2Cl6O. *Analytical Science, 22*, x127-x128.

Ratzlaff, J. D. (2004). Polyethylene. *Process Sensitivity in Rotational Moulding*. Retrieved from http://www.plasticmoulding.ca/polymers/polyethylene.htm

Sailors, H. R., & Hogan, J. P. (1981). History of Polyolefins. *Journal of Macromolecular Science: Part A - Chemistry, 15*(7), 1377-1402.

Sakai, S. (1991). A theoretical investigation of Ziegler-Natta polymerization reaction mechanisms of acetylene. *The Journal of Physical Chemistry, 95*(18), 7089-7093.

Sakai, S. (1994). Ab Initio Studies on the Ziegler-Natta Polymerization Reaction Mechanisms. The Role of Cocatalysis. *The Journal of Physical Chemistry, 98*(46), 12053-12058.

Schatschneider, B., & Perumareddi, J. R. (2005). UV–Vis absorption study of some tetragonal chromium (III) complexes. *Inorganica Chimica Acta, 358*(15), 4571-4574.

Soares, J. B. P., Kim, J. D., & Rempel, G. L. (1997). Analysis and Control of the Molecular Weight and Chemical Composition Distributions of Polyolefins Made with Metallocene and Ziegler−Natta Catalysts. *Industrial & Engineering Chemistry Research, 36*(4), 1144-1150.

Soga, K., Chen, S. I., Shiono, T., & Doi, Y. (1985a). Homo- and copolymerization of ethylene and propylene with a soluble chromium catalyst. *Polymer, 26*, 1888-1890.

Soga, K., Chen, S. I., Shiono, T., & Doi, Y. (1985b). Preparation of highly active Cr-catalysts for ethylene polymerization. *Polymer, 26*, 1891-1894.

Speetjens, J. K., Parand, A., Crowder, M. W., Vincent, J. B., & Woski, S. A. (1999). Low-molecular-weight chromium-binding substance and biomimetic [Cr3O(O2CCH2CH3)6(H 2O)3]+ do not cleave DNA under physiologically-relevant conditions. *Polyhedron, 18*(20), 2617-2624.

Theopold, K. H. (1998). Homogeneous Chromium Catalysts for Olefin Polymerization. *European Journal of Inorganic Chemistry, 1998*(1), 15-24.

Theopold, K. H., Heintz, R. A., Noh, S. K., & Thomas, B. J. (1992). Homogeneous Chromium Catalysts for Olefin Polymerization *Homogeneous Transition Metal Catalyzed Reactions* (Vol. 230, pp. 591-602): American Chemical Society.

Vlachos, A., Psycharis, V., Raptopoulou, C. P., Lalioti, N., Sanakis, Y., Diamantopoulos, G., Fardis M., Karayanni M., Papavassiliou G., Terzis A. (2004). A nearly symmetric trinuclear chromium(III) oxo carboxylate assembly: Preparation, molecular and crystal structure, and magnetic properties of $[Cr_3O(O_2CPh)_6(MeOH)_3](NO_3) \cdot 2MeOH$. *Inorganica Chimica Acta, 357*(11), 3162-3172.

Weckhuysen, B. M., & Schoonheydt, R. A. (1999). Olefin polymerization over supported chromium oxide catalysts. *Catalysis Today, 51*(2), 215-221.

Yazdanbakhsh, M., Lotfian, N., & Tavakkoli, H. (2009). Synthesis and characterization of two novel trinuclear oxo-centered, of chromium and iron complexes containing unsaturated carboxylate bridging ligand. *Bulletin of the Chemical Society of Ethiopia, 23*(3), 463-466.

Yazdanbakhsh, M., Tavakkoli, H., Taherzadeh, M., & Boese, R. (2010). Synthesis, X-ray crystal structure and spectroscopic characterization of heterotrinuclear oxo-centered complex $[Fe_2NiO(CH_3CH_2COO)_6(H_2O)_3]$. *Journal of Molecular Structure, 982*(1-3), 176-180.

Zhang, K. (2007). *Functionalized polyethylenes by combining chain walking polymerization and atom transfer radical polymerization.* M.A.Sc. dissertation, Laurentian University, Canada.