CHAPTER 1

INTRODUCTION TO ZIEGLER-NATTA POLYMERIZATION

1.1 INTRODUCTION TO POLYOLEFINS

Classical polymers such as polyethylene, polypropylene and polystyrene are of great interest for science and industry. Polyolefins are today among the most important commodity polymers. Due to the discovery of Ziegler-Natta catalysts and new technology processes, the polymer structure and the physical properties of polyolefins can be varied from soft elastomers to hard thermoplastics thus lead to a very broad range of applications.

Polyolefins are composed solely of carbon and hydrogen. Being thermoplastics, they can be easily processed. Used polyolefin materials can be recycled or combusted with a gain in energy and the only products left behind are carbon dioxide and water. The basic units, ethane and propane are easily obtained from cracking of petrochemical.

The most common commercial polyolefins are low-density polyethylene (LDPE), high-density polyethylene (HDPE), linear low-density polyethylene (LLDPE), polypropylene (PP), polystyrene (PS) and polyisobutylene (PIB). Among them, polyethylenes and polypropylenes are the major tonnage plastic materials worldwide.

In 2007, the global polyolefins demand exceeded 115 million tons, which was a growth of 5.3 percent over 2006. This was an outstanding growth and estimates show that this development will continue. Figure 1.1 shows global polyolefin consumption in 2007[1].

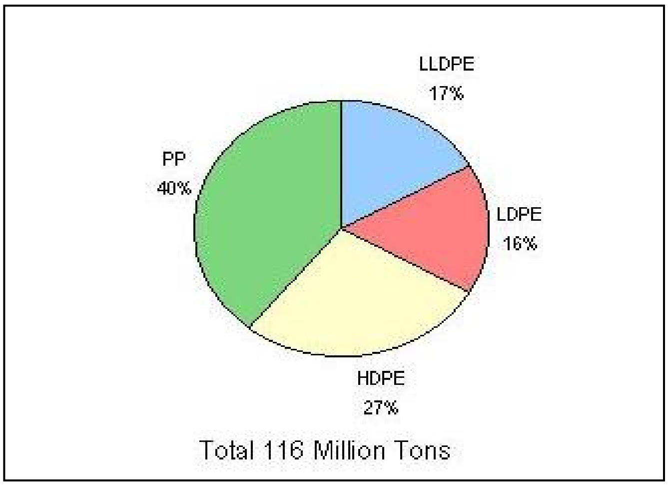


Figure 1.1: Global polyolefin consumption in 2007[1]

1.1.1 Polyethylene

Polyethylene (PE), a polymer consisting of long chains of the monomer ethylene is the most popular plastic worldwide. It is produced by polymerization of ethene thus its scientific name is *polyethene*[2,3].

PE is a versatile polymer that offers high performance relative to other materials. The molecular structure of PE affects the physical and chemical properties. There are three main categories of PE namely high density polyethylene (HDPE), low-density polyethylene (LDPE) and linear low–density polyethylene (LLDPE). The molecular structures of HDPE, LDPE and LLDPE are shown in Figure 1.2.

HDPE is mainly produced by Ziegler-Natta polymerization[4]. The molecules are linear or with very little branching. Absence of branching results in a more closely packed structure for the molecules. Therefore, material is rigid and strong in tensile strength. HDPE is normally manufactured with molecular weight in the range of 200,000-500,000 using low-pressure processes operated at 1 to 20 atmospheres. The density of a high-density polyethylene usually varies from $0.94 gcm^{-3}$ to $0.97 gcm^{-3}$. More than 75%-90% of the materials are crystalline. HDPE is chemically inert and permeable to gas. Major uses of high-density polyethylene include making of water pipes, wire and cable insulation, plastic containers and freezer bags.

LDPE is a highly branched polymer with density varies from 0.91gcm^{-3} to 0.935gcm^{-3}. The main chain contains many branching leading to irregular packing and low crystallinity. LDPE is often made by free radical polymerization at high temperature and pressure. LDPE is more flexible and less tensile strength as compared to HDPE. It has good resistance to acids and alkalis. LDPE is widely used for manufacturing various containers, washing bottles, plastic bags and molded laboratory equipments.

LLDPE is produced by copolymerization of ethylene with relatively small amounts of 1-alkene at low temperature. The copolymerization process generates short branches along the linear polyethylene chain. The densities of LLDPE vary from 0.926gcm^{-3} to 0.94gcm^{-3}. LLDPE has higher tensile strength and higher impact resistance than LDPE. Major applications of LLDPE are plastic bags, pouches, toys, lids and mainly flexible tubing.

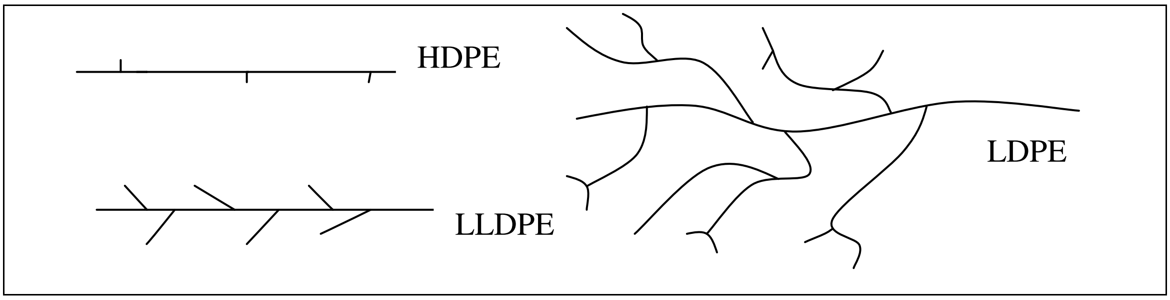


Figure 1.2: The molecular structures of HDPE, LDPE and LLDPE

The density of polyethylene has significant effect on many physical properties. Increase densities result in increased tensile strength, hardness, stiffness and resistance to heat. However, elongation decreases when the density increases.

1.2 Polypropylene (PP)

Polypropylene is a thermoplastic with a linear structure based on the monomer C_3H_6. It has been used widely in industry and in consumer goods. The first polypropylene resin was produced by Giulio Natta in Spain, and the commercial production of PP began in 1957. Polypropylene can be manufactured by Ziegler-Natta polymerization and by metallocene catalysis polymerization[5,6].

The repeating unit of polypropylene contains an asymmetric carbon, which gives rise to stereospecific configurations. The three possible configurations are isotactic, syndiotactic and atactic. Most commercial polypropylene is isotactic which is geometrically regular and is highly crystalline.

PP plastics can be categorized into three groups which are (i) the unmodified homopolymer, (ii) the modified popypropylene and (iii) the PP copolymers. The unmodified homopolymer is the oldest variety and is produced in the largest scale. The unmodified PP consists of mixing a filler such as asbestos or a graphite fibre. The PP copolymers account about one third of the polypropylene market are normally produced by using ethylene as comonomer. The copolymers can be divided into random type and block type. They are frequently referred to as medium- or high- impact PP, depending on the structure and the amount of ethylene comonomer used.

Polypropylene is commonly used in our daily life. PP homopolymers have better resistance to stress and cracking, better chemical resistance, better clarity and gloss, lower gas permeability and lower thermal expansion than PE.

PP homopolymers have higher operational temperature with a melting point of 160°C compared to PE. Besides, PP has higher tensile strength, surface hardness and flexural strength than HDPE. PP has excellent dielectric properties and it is highly resistant to most alkalis, acids and organic solvents. It is also non-toxic and non-staning.

However at below the room temperature, PP homopolymers have poor impact strength. This can be overcome by PP copolymers. PP has been modified by the incorporation of fillers to improve properties such as less heat distortion and improved stiffness. Extrusion and injection molding are the two biggest application processes for polypropylene.

Major products by extrusion process include fibers, filaments, films, sheets and coating for wire and piping. Randomly polymerized ethylene monomer which added to PP homopolymer decreases the polymer crystallinity and makes the PP film more transparent and clear. PP bottles have an advantage over the PVC bottles as they do not create pollution problems when the bottles are disposed of by burning. Therefore, PP bottles have been widely used for packaging of cosmetics, pharmaceuticals, mouthwashes and detergents.

PP is injection-molded into housewares, toys, laboratory and medical appliances. Filled polypropylenes are molded to produce automotive fan shrouds and car bumpers. High-impact PP is molded to manufacture luggages, seating parts, battery cases, protective shielding and automotive kick panels.

Polypropylene is commonly recycled. Table 1.1 shows major plastic recycling codes[7].

Table 1.1: Recycling codes of major plastic resins[7]

Resin Code	Name	Uses
♳ PET	Polyethylene Terephthalate	Plastic drinks bottles, cooking oil bottles, peanut butter and salad dressing containers
♴ HDPE	High Density Polyethylene	Detergent bottles, milk jugs, water pipes
♵ PVC	Polyvinyl Chloride	Plastic pipes, outdoor furniture, shrink wrap, water bottles, salad dressing containers
♶ LDPE	Low Density Polyethylene	Dry cleaning bags, produce bags, food storage container
♷ PP	Polypropylene	Bottle caps, drinking straws, food trays, outer containers
♸ PS	Polystyrene	Packaging pellets, cups, food trays
♹ OTHER	Other	Additional plastic polymers not listed under 1-6 above, certain types of food containers including tupperware

1.2 Production Process of Polyolefins

Production of polyolefins is a multi-billion business. Commercial processes used for polyolefin production include solution process, slurry process and gas-phase process.

The solution process uses an inert hydrocarbon that dissolves the polymer as it is formed. Monomer and polymer remain in the solution during the reaction while the catalyst is maintained in suspension by agitation. Mitsui Petrochemicals[8] has announced the production of medium density polyethylene presumably by copolymerizing small amounts of α-olefins. Special Ziegler catalysts are used for this process[9]. Polymerization by solution process has the advantage from the standpoint of heat removal and control. High density polyethylene and linear low-density can be produced using solution reactor, the second oldest method of polyethylene production. Medium pressures (500 psi) and temperature 160°C to 200°C are used in the reaction. Reproducible product with low molecular weight can be obtained in solution process. However, the yield is low.

Slurry process is an important polymerization method to produce high molecular weight polymers[9-10]. It often employs a diluent of a poor solvent for the polymer. The solvent keeps both catalyst and polymer in suspension during polymerization. Slurry polymerization is carried out in batch reactor where the monomer, solvent, chain transfer agent and catalyst are fed continuously to the reactor. Looped type slurry reactor uses isobutene as the diluents while stirred tanks type uses hexane. Both systems operate at temperature 70°C to 110°C and pressure less than 700 psi. The slurry and bulk processes are the most important polymerization process at the present, amidst efforts on the development of gas-phase polymerization processes.

The gas-phase polymerization process is the most efficient method to produced polyolefin. Polymerization run is carried out in the vapour phase under moderate pressure and temperature without the presence of a dispersant. The catalyst particles are distributed throughout the monomer during the reaction. Examples of polymerization using gas-phase reactor are UNIPOL 1 process and Novolen Process (BASF).

In most cases, the choice of the production process is very much dependant on the catalyst system used and the targeted product properties. Therefore, considerations need to be taken in order to obtain polymers with favourable product yield.

1.3 Types of Catalysts

Catalysts can be divided into homogeneous and heterogeneous catalysts. In a homogeneous reaction, the catalyst is in the same phase as the medium of reaction. Typically the catalyst and reactants will be present as a gas or contained in a single liquid phase. Examples of homogeneous catalyst include vanadium based catalyst and metallocene catalyst.

In a heterogeneous catalyst reaction, the catalyst is in a different phase from the medium of reaction; an example would be titanium based catalyst. Heterogeneous catalysts provide a surface for the chemical reaction to occur. Usually the catalyst is in a solid phase while the reactants are liquid or gases. A heterogeneous reaction happens when one or more reactants are adsorbed on the catalyst at active sites. Then, interaction occurs between the reactants molecules and catalyst surface which makes them more reactive. In the final stage, the product molecules desorbed where the molecules break away and leave the catalyst active sites available for new molecules to attach to and react. In the production of polyolefins except LDPE, either homogeneous or heterogeneous catalysts are employed. Polyolefins such as HDPE, LLDPE and PP are produced by using catalysts and polymerization reactions are operated at low temperature (80-100°C) and low pressure (< 50bar). For LDPE, radical combination reactions occur at relatively high temperature (250-300°C) and pressure (> 50bar). In almost all catalyzed polymerization reactions, the catalyst is used and a part of catalyst comes into polymer chains in the initiation and/or termination step.

Olefin polymerization catalysts can be divided into a four groups which are (i) Philips-type catalysts, (ii) Ziegler-Natta catalysts, (iii) molybdenum oxide catalyst and (iv) metallocene catalysts. Philips catalysts or so called chromic catalysts are prepared by impregnating 1 to 3 percent of chromic oxide on support such as silica or silica-alumina. It yields bimodal polyethylene with good mechanical properties and good processability[11].

A Ziegler-Natta catalyst is formed by reacting a metal alkyl or alkyl halide with a transition metal salt[12]. The catalysts are widely used for the commercial production of high density polyethylene (HDPE). Most polymers produced using heterogeneous Ziegler-Natta catalysts are with broad molecular weight distribution.

Molybdenum catalysts have been described as hydroforming catalysts which contain up to 8 percent of molybdenum oxide supported mainly alumina[13]. The catalysts are mainly used in solution process and polyethylene produced by this catalyst has an unannealed density (0.958 – 0.960 gcm^{-3}).

Metallocene catalysts[14] are based on metallocene of group 4 transition metals with methylaluminoxane (MAO). The catalysts exhibit a high activity for olefin polymerization and this catalyst system allows properties of the polymer produced to be tailored in many ways[15]. The custom properties include greater stiffness and impact strength, greater stretch and improved sealability. Although metallocene catalysts show many advantages, the polymers produced have a very narrow molecular weight distribution.

1.4 Ziegler-Natta Catalysts

Ziegler-Natta catalysts have been defined as the products of reaction between compounds of transition elements of groups IV to VIII (titanium, vanadium or zirconium halides) and compounds such as the hydrides or alkyls of groups I-III[12] such as $LiEt_3$, $BeEt_3$, $AlEt_3$ or $AlEt_2Cl$. In common practice, the transition element component is called the catalyst whilst the hydride or alkyl is referred to cocatalyst[16-17].

1.4.1 Historical Development of Ziegler-Natta Catalysts

In 1953, Ziegler and his co-workers[17-21] accidentally discovered the activity of nickel as a catalyst in reactions of ethylene with aluminium alkyls. A linear polyethylene with high molecular weight was formed at normal ethylene pressure and at low temperatures. Following that, investigation was taken by Ziegler and his co-workers to determine what other metals might show the same activity[18,22]. Results showed that compounds of the transition metals of group IV – VII especially titanium, when combined with aluminium alkyls, are effective polymerization catalysts.

After Ziegler and his co-workers' discovery of the low-pressure polymerization of ethylene, Natta, an Italian chemist has published a series of papers showing that higher olefins like propylene and 1-butene were able to be produced using Ziegler's catalysts[23-25]. Isotactic polypropylenes with high strength and high melting points were obtained and the polymers were stereoregular. Since then, these catalysts became known as Ziegler-Natta catalysts.

The Ziegler-Natta catalysts contributed to the development of the long chain polymers of hydrocarbons. These polymers are useful in the manufacture of plastics, fibres and films. Thus in 1963, Ziegler and Natta were honoured with the Nobel Prize for Chemistry.

Ziegler-Natta catalysts have evolved to the four generations[26]. Titanium chloride and diethylaluminium as cocatalyst were used in the first generation. Polymerization using $TiCl_3$-$(C_2H_5)AlCl$ system generated polymers of 90% isotactic and the catalyst residues were deactivated using TiO_2. The second generation catalysts[26-27] used titanium chloride/$AlEt_2Cl$ plus an internal electron donor such as ether and ester increased the catalysts activity and stereo specificity.

In 1968, the third generation catalysts were introduced[28-30]. The catalyst system consists of complexes of $TiCl_4$ supported on $MgCl_2$. This system is able to yield linear polyethylene and isotactic polypropylene. No removal of the catalyst residues from the final product is needed. The fourth generation[31-32] catalysts used homogeneous catalysts for olefin polymerization. The catalyst system is based on metallocene compounds and leads to different polymer properties. The chronological developments of Ziegler-Natta catalysts are summarized in Table 1.2.

Table 1.2: Chronology of development in Ziegler-Natta catalysis

Generation	**Catalyst**	**Support**	**Process Steps**
First generation	$TiCl_3/AlEt_2Cl$	-	Remove catalyst residues
Second generation	$TiCl_3$/ether/$AlEt_2Cl$/ester	-	Remove catalyst residues
Third generation	$TiCl_4$	Activated $MgCl_2$	No purification
Fourth generation	Al-oxame activated metallocene complexes	Silica gel	No purification No palletizing extrusion

1.4.2 Applications of Ziegler-Natta Catalysts in Olefin Polymerization

Many catalyst systems have been described since the discoveries by Ziegler and Natta. The typical Ziegler-Natta catalysts are combinations of triethyaluminium ($AlEt_3$) or diethylaluminium ($AlEt_2Cl$) with titanium tetrachloride ($TiCl_4$) or trichloride ($TiCl_3$).[16] These catalyst systems are usually heterogeneous.

Preparation of heterogeneous catalyst may be done in two methods. In the original Ziegler method[33], hydride or alkyl compound from the base metal group was mixed with the transition element (eg. titanium tetrachloride), which was in its highest valence set. Polymerization using this method produced polymers of low molecular weight[34] which is less satisfactory for α-olefins. Further work done by Natta and his co-workers successfully discovered the first highly stereospecific catalytic systems for the polymerization of α- olefins[35]. The use of transition metal compound in a lower valency state Ti(III) managed to give polyolefins in good yield with high molecular weight and high degree of stereoregularity[36-37].

Majority of uses of Ziegler-Natta catalysts are for polymerization. The most common olefins polymerized are ethylene, propylene, 1-butene , 1-hexene and 1-octene. Ziegler-Natta catalysts are commercially used by the industries to prepare stereoregular polymers. This catalyst system occurs at mild polymerization conditions (at normal room temperature and under atmospheric pressure).

Ziegler-Natta catalysts can be used to produce HDPE which appears to have the largest market among all polyolefins. Ziegler-Natta catalysts are also involved in the production of stereoregular polypropylene. Various suitable combination of Ziegler-Natta catalysts yield polypropylene with different tacticity and favorable uses. LLDPE can be obtained by co-polymerizing ethylene with 1-alkene using Ziegler-Natta catalysts.

Other applications of Ziegler-Natta catalysts include the production of ultra-high molecular weight polyethylene (UHMWPE), thermoplastic polyolefins (TPO's), ethylene propylene diene monomer polymers (EPDM) and polybutene (PB). Ziegler-Natta catalysts remain dominant in production technology for polyolefins due to significant cost benefits and low cost of polymers.

1.4.3 Chromium Based Polymerization Catalyst

Many catalyst systems have been investigated since those originally discovered by Ziegler and Natta. Chromium salts were found to have catalytic activity in ethylene and propylene polymerization[4]. Among those were chromium(II) chloride, $CrCl_2$, chromium(III) chloride, $CrCl_3$ and chromium(III) acetate, $Cr(acac)_3$[37-38]. However, they were less effective as polymerization catalysts compared to others Ziegler-Natta compounds.

Philips catalysts have gained much attention in commercial polymerization industries. The Philips polymerization catalyst is typically prepared by impregnating a chromium compound onto a high surface area and wide pore carrier, usually silica, and then calcining in dry air or oxygen to ‘activate’ the catalyst[39]. Philips catalysts are the main catalysts used to produce high density polyethylene worldwide.

A new chromium catalyst have been prepared by Battelle by reacting $Cr(CH_3COO)_3H_2O$ with acetic acid and acetic anhydride[40]. This catalyst when combined with diethyaluminium chloride ($AlEt_2Cl$), gives high activity in ethylene polymerization. Gan et al.[41-42] reported that $Cr(CH_3COO)_3$ catalyst can be used in both the homopolymerization of ethylene and random co-polymerization of ethylene and propylene. They also reported that the same catalyst can be prepared by different starting materials[43]. Later, K. Soga et al.[44] successfully modified the Batelle-type catalyst and improved the polymerization activity. The modified catalyst was stable in air and soluble in usual organic solvents.

Other chromium based catalysts used in the polymerization of ethylene are bis(triphenylsilyl) chromate supported on silica[45] and chromocenes[46]. Peuker et al.[47] found that a new class of homogeneous chromium based catalysts were active in vinylic polymerization. A catalyst system comprising of $Cr(acac)_3/MgCl_2$-BEAC-EB synthesized by Yong et al.[48] successfully produced ethylene-propylene random copolymers.

Recently, complexes of transition metals with polydentate nitrogen-containing ligands showed promising results in olefin polymerization[49-50]. Semikolenova and co-workers[51] showed that chromium bis(arylimino)pyridine complexes were active in polymerization to yield highly linear polyethylene.

1.4.4 Diethylaluminium Chloride as Cocatalyst

Alkyl or hydride compounds from groups I-III, or oftenly called cocatalyst, are one of the two major components in Ziegler-Natta catalysts. Natta discovered that the more electropositive elements from the base metal groups are the more active as cocatalyst[52].

In a Ziegler-Natta system, a cocatalyst acts as a chain transfer agent[16]. A cocatalyst activates the sites on the catalyst. It forms a complex with the catalyst site and makes them active for polymerization. Aluminium alkyls are normally used as the cocatalysts in Ziegler-Natta polymerization.

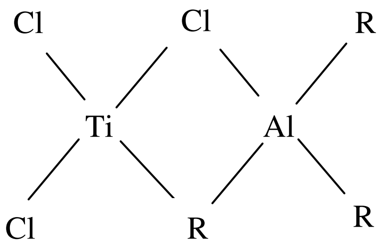
In the study of ethylene polymerization using chromium stearate catalyst system in the presence of various alkyl aluminium, Soga and co-workers[53] reported that diethylaluminium chloride, $AlEt_2Cl$ showed the highest activity. Aishah[54] observed that the catalytic activity increased in the order of $AlEt_3 < i\text{-}BuAlCl_2 < AlEt_2Cl$ during the polymerization of ethylene. The observed order of activity could be due to the relative reduction power of the aluminium alkyls.

Diethylaluminium chloride is a clear liquid in room temperature with melting point -74°C and a high boiling point 208°C. It ignites spontaneously on contact with air and reacts violently when it is in contact with water. Therefore extreme care is needed when handling reactions involved aluminium chloride.

1.5 Mechanism of Ziegler-Natta Polymerization

Some of the polymerization mechanisms proposed during the earlier years were centered around free radical propagation[55]. The concentration of radicals lies below the sensitivity limit of electron spin resonance. Other two possible reaction mechanisms investigated were coordinated cationic and coordinated anionic propagation. Since the publication by Natta and co-workers[36], many researchers favored the coordinated anionic mechanism.

Generally, two mechanisms have been proposed in Ziegler-Natta polymerization. Furukawa et al.[56] proposed a polymerization centre involving two metal atoms, as shown in Figure 1.3. It was suggested in this bimetallic structure, the Al atom donates electron while the Ti atom acts as an electron acceptor.



where R = alkyl

Figure 1.3: Bimetallic Structure[56]

A bimetallic mechanism was first proposed by Natta[57] and it received considerable support. Natta and co-workers suggested the propagation from an aluminium centre in a bimetallic complex. Natta et al.[58] studied ethylene polymerization using the soluble bimetallic complex shown in Figure 1.4.

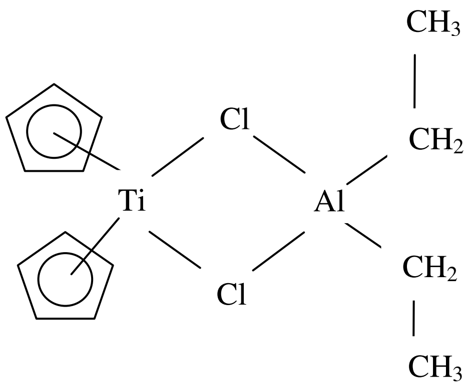


Figure 1.4: Bimetallic complex used by Natta et al.[58] for ethylene polymerization

According to Natta and co-workers, the transition metal compound reacts with aluminium alkyls to form a soluble complex. The Ti-polymer partial bond of the complex is broken during the insertion of ethylene monomer. The monomer was initially coordinated onto the Ti atom. The Ti atom was activated and the monomer was then transferred to Al atom. Patat and Sinn[59] has also proposed the same mechanism for the polymerization of ethylene. The suggested mechanism is shown in Figure 1.5.

Other researchers who favored a bimetallic mechanism include Huggins[60] and Boor[61].

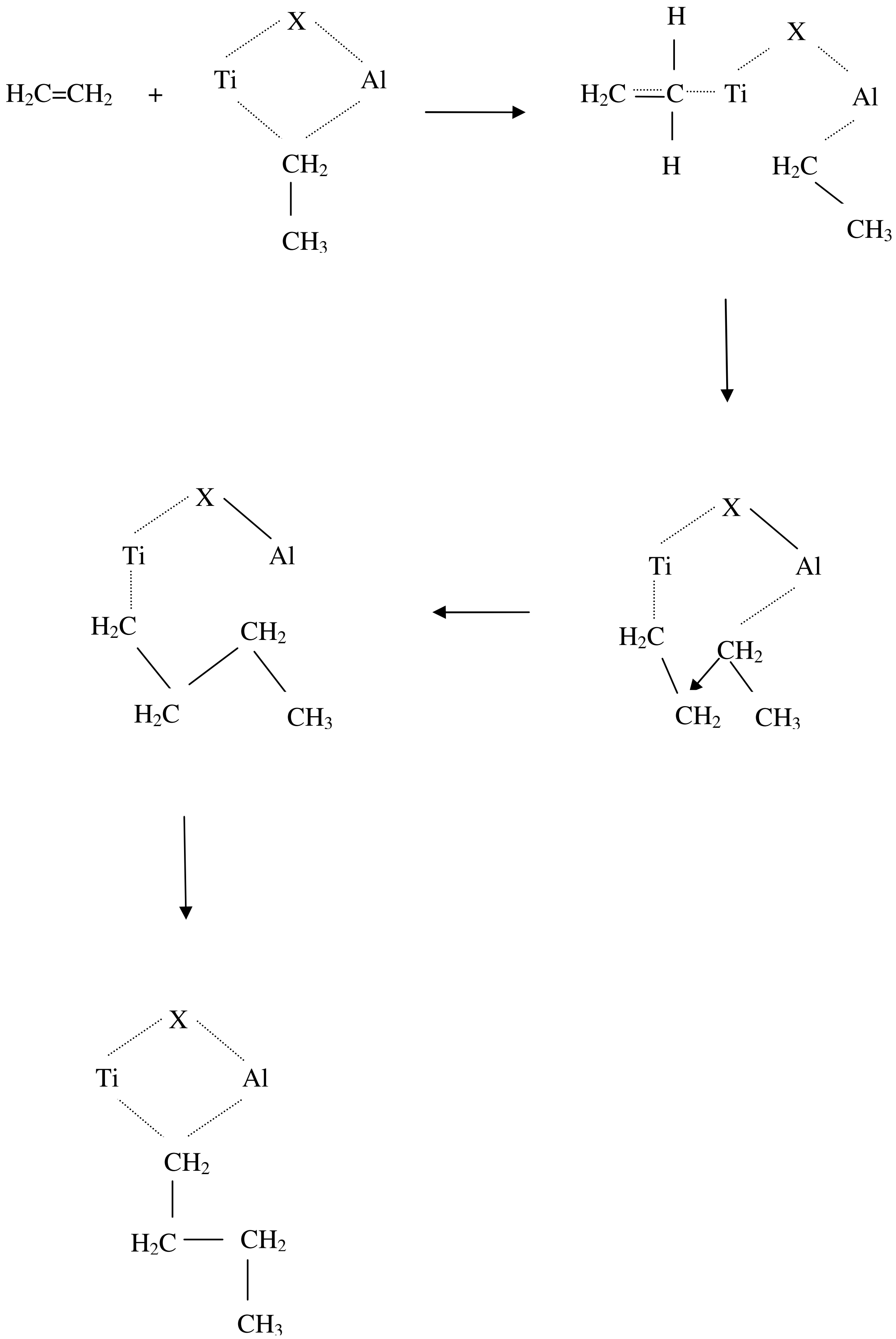
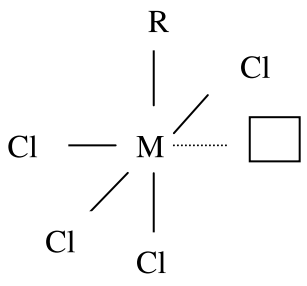


Figure 1.5: Bimetallic mechanism for ethylene polymerization[59]

In contrast to bimetallic mechanisms, monometallic polymerization mechanisms involve only one metal atom in the propagation step. It was assumed that the transition metal atom acts as the polymerization centre, while the metal alkyl alkylates the centre.

A number of kinetic studies of heterogeneous catalyst systems indicated that a monometallic mechanism is preferable. Cossee[62] proposed a monometallic model as shown in Figure 1.6 and described the formation of the active centre. He then suggested the monometallic mechanism for polymer chain growth and this mechanism had gained much attention in the field of polymerization studies.



where R = growing polymer chain
M = transition metal
□ = vacant orbital for coordination

Figure 1.6: Monometallic structure[62]

In a monometallic structure, the transition metal is surrounded by four ligands, one alkyl group and a vacant site. This octahedral transition metal forms the active centre of the structure. One growth step in Cossee's mechanism is shown in Figure 1.7.

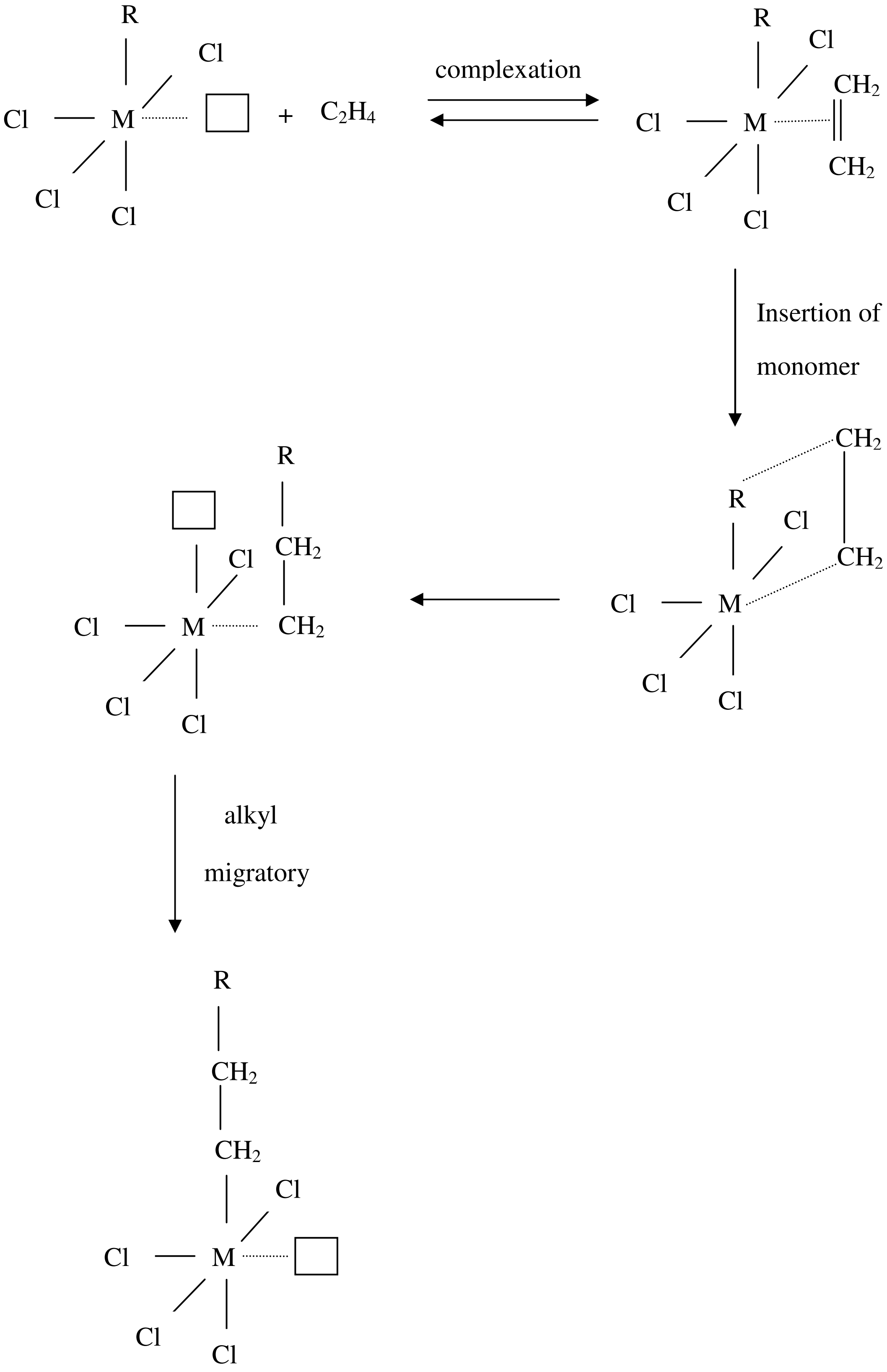


Figure 1.7: Ethylene polymerization mechanism[62]

Cossee[62] supposed that active centre formation was due to the interaction between metal alkyl and the vacant site. A monomer unit adsorbed on the transition metal and formed a π-bond with the transition metal. The bond between transition metal and alkyl broke thus generated a new vacancy. The growing alkyl group and the new vacancy exchange their position to restore the original arrangement of the active site.

1.6 Kinetics of Ziegler-Natta Polymerization

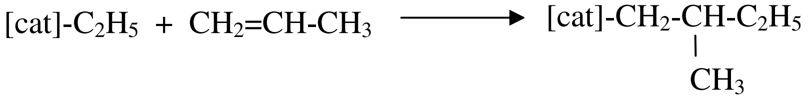
The kinetics of Ziegler-Natta polymerization have provided useful information in the formulation of models or reactions mechanisms to polymer scientists since the first discovery of these catalysts. Blais and Manley[63] presumed that the changes of the polymerization conditions have an influence on the polymers produced by affecting the polymerization rate.

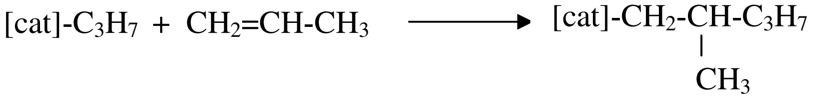
Factors that affect the kinetic results can be categorized into three groups, which are (i) those related to catalyst, (ii) those related to polymerization and (iii) those related to third components such as transfer agents, reactants and electron donors. Factors related to catalysts include choice of catalyst components, stability, concentration of components and order of mixing. Concentration of monomer, type of solvent, polymerization time and temperature, polymer yield and competing reactions are operational factors related to polymerization.

Natta and co-workers[64] had proposed a kinetic scheme for Ziegler-Natta polymerization which involves three different steps: initiation, propagation and termination. The reactions proposed by Natta and co-workers are shown below.

Initiation

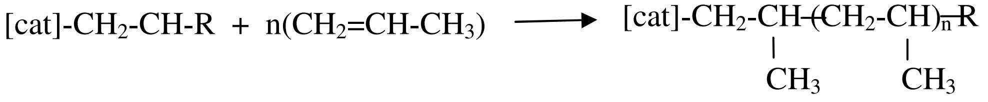
1. $\mathrm{[cat]\text{-}H + CH_2{=}CH\text{-}CH_3 \longrightarrow [cat]\text{-}C_3H_7}$

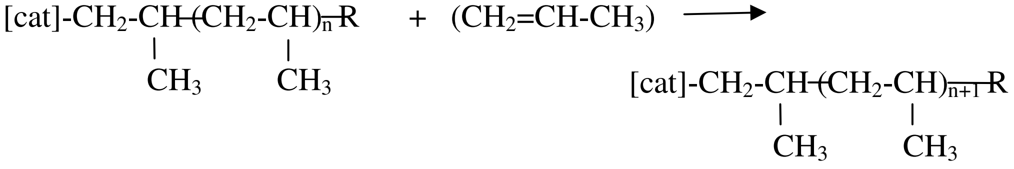
2. 
$$\mathrm{[cat]\text{-}C_2H_5 + CH_2{=}CH\text{-}CH_3 \longrightarrow [cat]\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}C_2H_5}$$

3. 
$$\mathrm{[cat]\text{-}C_3H_7 + CH_2{=}CH\text{-}CH_3 \longrightarrow [cat]\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{C}}H\text{-}C_3H_7}$$

where [cat]-H and [cat]-R denote the active centres. The centre is active if R is a polymer chain, a hydride or an alkyl.

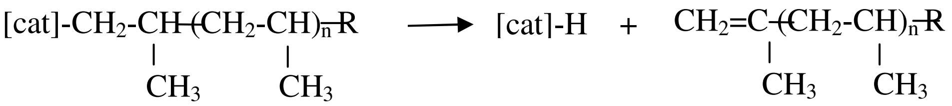
Propagation

4. 
$$\mathrm{[cat]\text{-}CH_2\text{-}CH\text{-}R + n(CH_2{=}CH\text{-}CH_3) \longrightarrow [cat]\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}})_n\text{-}R}$$

5. 
$$\mathrm{[cat]\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}})_n\text{-}R + (CH_2{=}CH\text{-}CH_3) \longrightarrow [cat]\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}})_{n+1}\text{-}R}$$

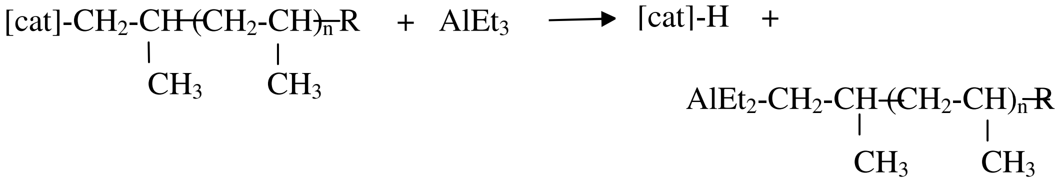
Chain Termination

Dispropotionation

6. 
$$\mathrm{[cat]\text{-}CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}}\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}})_n\text{-}R \longrightarrow [cat]\text{-}H + CH_2{=}\underset{\displaystyle CH_3}{\underset{|}{C}}\text{-}(CH_2\text{-}\underset{\displaystyle CH_3}{\underset{|}{CH}})_n\text{-}R}$$

Transfer by Base Metal Alkyl ($AlEt_3$)

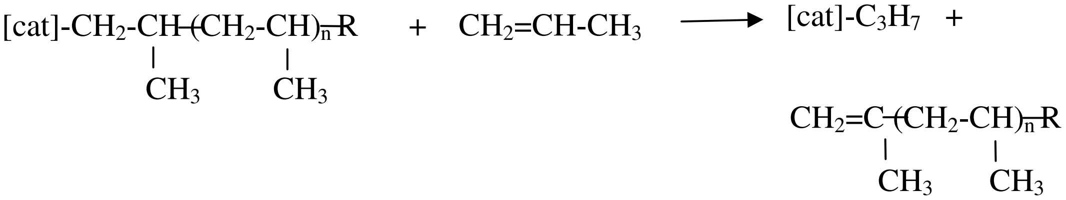
7.



$$\text{[cat]}-CH_2-\underset{\underset{CH_3}{|}}{CH}-(CH_2-\underset{\underset{CH_3}{|}}{CH})_n-R + AlEt_3 \longrightarrow \text{[cat]}-H + AlEt_2-CH_2-\underset{\underset{CH_3}{|}}{CH}-(CH_2-\underset{\underset{CH_3}{|}}{CH})_n-R$$

Transfer by Monomer

8.

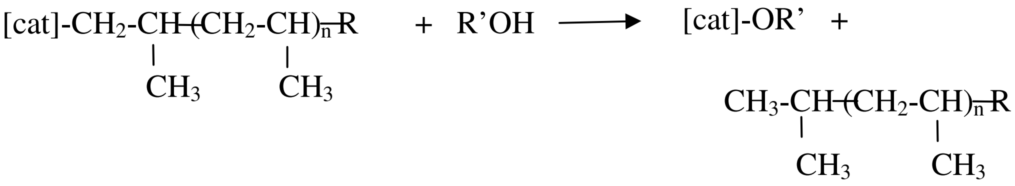


$$\text{[cat]}-CH_2-\underset{\underset{CH_3}{|}}{CH}-(CH_2-\underset{\underset{CH_3}{|}}{CH})_n-R + CH_2=CH-CH_3 \longrightarrow \text{[cat]}-C_3H_7 + CH_2=\underset{\underset{CH_3}{|}}{C}-(CH_2-\underset{\underset{CH_3}{|}}{CH})_n-R$$

In all of the termination reactions, the chain growth stops, but the [cat]-R remains active for further polymerization. However, in the presence of impurities, termination of chain growth will be accompanied by inactivation of the centre, as shown in the equation below.

Inactivation of Active Centre

9.



$$\text{[cat]}-CH_2-\underset{\underset{CH_3}{|}}{CH}-(CH_2-\underset{\underset{CH_3}{|}}{CH})_n-R + R'OH \longrightarrow \text{[cat]}-OR' + CH_3-\underset{\underset{CH_3}{|}}{CH}-(CH_2-\underset{\underset{CH_3}{|}}{CH})_n-R$$

Eirich and Mark[65] first pointed out that, since most of the Ziegler-Natta catalyst systems were of heterogeneous nature, adsorption processes were involved in the reaction mechanism. The concepts were then used by Saltman[66], Kern et al.[67] and Keii et al.[68]. However, their findings did not explain the maxima in rate observed during the reactions.

Otto and Parravano[69] suggested that propagation occurs between adsorbed monomer and an alkylated transition metal. Burfield[70] then elucidated this idea and proposed a kinetic scheme using VCl_3/AlR_3/4-methyl-1-pentene system. In the proposed scheme, propagation is considered to occur with an active centre formed by interaction of the metal alkyl with the transition metal halide. The polymerization rate is expressed in

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

where k_p is the propagation rate constant with respect to adsorbed monomer, θ_M is the fraction of the surface covered by adsorbed monomer and C_o is the active centre concentration. Considered competitive adsorption between monomer, M and metal alkyl, A and active centres, S,

$$S + M \xleftrightarrow{K_M} S \ldots M$$

$$S + A \xleftrightarrow{K_A} S \ldots A$$

The fraction of active centres with adsorbed monomer (θ_M) and the fraction with adsorbed alkyl (θ_A) may be expressed in terms of Langmuir-Hinshelwood isotherms as:

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

and

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

where [M] and [A] are the concentrations of monomer and metal alkyl, while K_M and K_A are the equilibrium constants for the equilibria. Thus the rate of polymerization becomes

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

1.7 Copolymerization

Copolymerization of ethylene and α-olefins[71-72] have been demonstrated soon after the discovery that Ziegler-Natta catalysts homopolymerize α-olefins. Copolymers have gained much interest in polymer field due to their elastomeric characteristics. Therefore, many research works were carried out to prepare better catalyst systems and to obtain more interesting elastomeric copolymers.

The properties of the copolymers formed can be controlled by operating conditions, chemical composition and physical state of catalyst and comonomers structure. The most important copolymer is prepared from ethylene and propylene. The production of ethylene-propylene copolymers were traditionally carried out with homogenous Ziegler-Natta catalyst based on vanadium compounds.[73-74] The application of the Ziegler-Natta heterogenous catalytic system based on titanium compounds for the production of copolymers has recently become more important, due to high activity of the catalyst systems and low production costs.[75-76]

The best coordinated anionic type catalyst suitable for the production of ethylene-propylene copolymers are obtained by reaction of alklyaluminium compounds with transition metals such as vanadium, chromium, niobium and titanium. Recently, Soga and coworkers[53] successfully copolymerized ethylene and propylene using a soluble chromium catalytic system composed of $Cr(C_{17}H_{35}COO)_3$ and $AlEt_2Cl$. The catalytic system produced random copolymer with a narrow molecular weight distribution.

1.8 Kinetics of Copolymerization

When two or more monomers are present in a copolymerization mixture, each must compete with the others for the available centers. In 1944, Alfrey and Goldfinger[77] proposed four separate propagation reactions in the copolymerization of two vinyl monomers.

$$M_1^* + M_1 \xrightarrow{k_{11}} M_1^*$$

$$M_1^* + M_2 \xrightarrow{k_{12}} M_2^*$$

$$M_2^* + M_2 \xrightarrow{k_{22}} M_2^*$$

$$M_2^* + M_1 \xrightarrow{k_{21}} M_1^*$$

where k_{ij} refers to the characteristic propagation rate constant, M_1 and M_2 are the two monomers and M_1^* and M_2^* are the growing polymer chain ends terminated by M_1 and M_2, respectively.

Copolymerization equation has the form shown below,

$$\frac{d[M_1]}{d[M_2]} = \frac{[M_1]\,(\,r_1\,[M_1] + [M_2]\,)}{[M_2]\,(\,[M_1] + r_2\,[M_2]\,)}$$

where r_1 and r_2 are reactivity ratios, $[M_1]$ and $[M_2]$ are instantaneous concentrations of the two monomers and $d[m_1]/d[m_2]= m_1/m_2$ is the molar ratio of the two monomer units in the copolymer.

According to Odian[78], first-order Markov statistics have been applied to characterize the kinetics of olefin copolymerization. The monomer reactivity ratios, r_1 and r_2 are defined as the ratio of the homopropagation rate constant (r_{ii}) to the cross-propagation rate constant (k_{ij}).

$$r_i = k_{ii} / k_{ij}$$

thus,

$$r_1 = k_{11} / k_{12}$$

$$r_2 = k_{22} / k_{21}$$

From the product r_1r_2, the type of monomer distribution in the copolymer can be determined.[79] $r_1 = r_2 = 1$ indicates a random distribution along the copolymer chain. If $r_1 > 1$ and $r_2 > 1$, the copolymer has a block character. If $r_1 < 1$ and $r_2 < 1$, the catalyst has tendency to alternate the comonomers in the copolymer chain.

1.9 Trinuclear Oxo-Centered Complex

Trinuclear oxo-centered complexes, have the general formula $[M_3O(RCO_2)_63L]^+$ where M= metal atoms, R= alkyl or substituted-alkyl and L= monodentate ligands. The general structure is shown in Figure 1.8. Weinland[80] synthesized the first trinuclear basic acetates using chromium(III) and iron(III). X-ray diffraction method was used to study the structure of trinuclear oxo-centered complexes and the first reported structure was $[Cr_3O(CH_3CO_2)_6(H_2O)_3]Cl.6H_2O$[81].

Synthesis of the trinuclear oxo-centered complexes can be done in many ways. Johnson et al.[82] prepared chromium(III) trinuclear complexes by refluxing freshly precipitated chromium(III) hydroxide with carboxylic acid for 2 hours. The preparation method described by Earnshaw et al.[83] involved the reaction of metal salt with the sodium salt of the appropriate carboxylic acid. Ever since then, this method was used by other workers to prepare oxo-complexes of vanadium and iron[84-85].

Recently, Gan et al.[43] have shown that chromium based trinuclear oxo-carboxylate complexes can be used in producing propylene of high isotacticity and random copolymers of ethylene and propylene. The complexes, with the general formula $[Cr_3O(RCOO)_6.3H_2O]NO_3.nH_2O$ where R= alkyl or chloro substituted alkyl and n= number of hydrated water molecules were prepared by refluxing commercial chromium(III) nitrate nonahydrate with glacial acetic acid or chloro substituted acetic acid.

X-ray crystallography has been widely used in determining the structure of trinuclear complexes which could be successfully crystallized. Other characterization methods include infrared spectroscopy[86-87], magnetic susceptibity measurement[83,88] and thermal analysis[89-90].

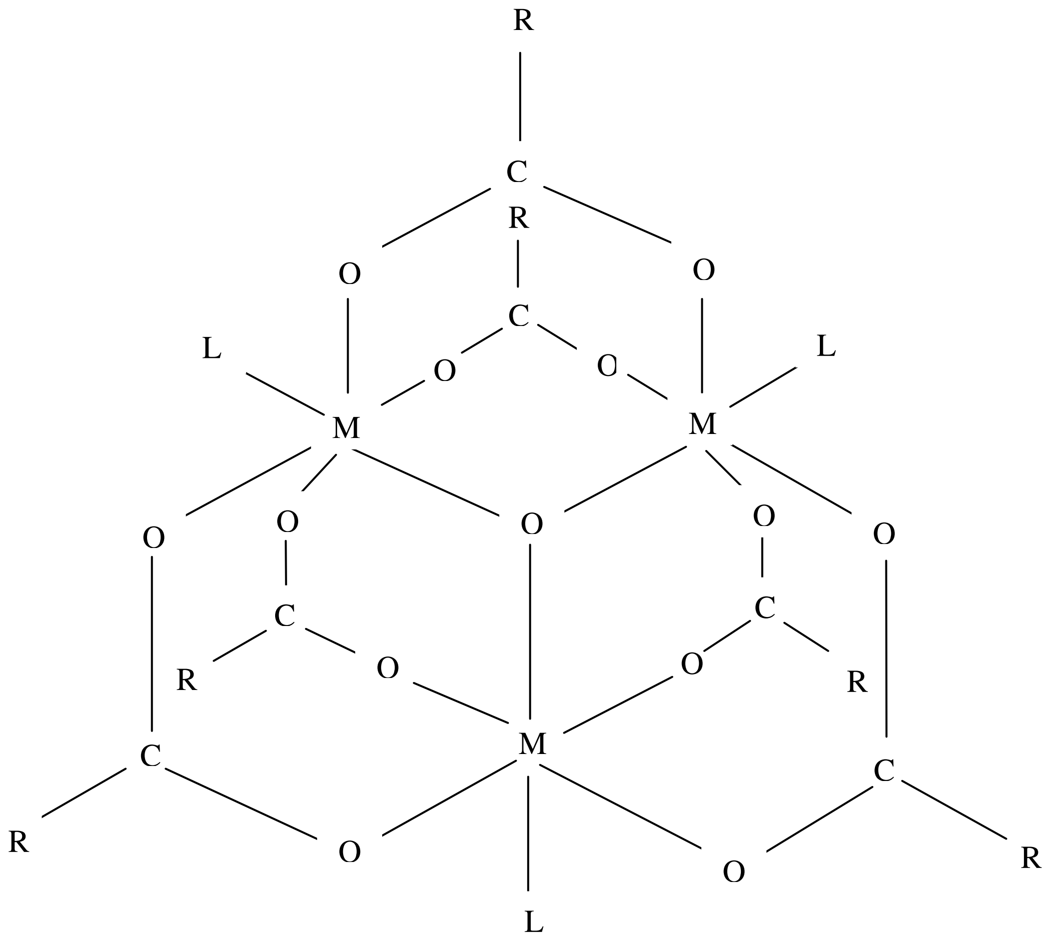


Figure 1.8: Trinuclear carboxylate structure, $[M_3O(RCO_2)_63L]^+$

1.10 Scope of This Study

Chromium based Ziegler-Natta catalysts have been reported to show activities in the polymerization of olefins such as ethylene and propylene. Preparation of chromium based catalysts were carried out by many researchers since Batelle patented $Cr(CH_3COO)_3$ complex.

This study used chromium based oxo-trinuclear carboxylate complexes in combination with aluminium alkyls to form catalysts for the polymerization of ethylene and propylene. Chromium(III) nitrate nonahydrate was treated with excess chloroacetic acid to form $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ complex. Other chromium(III) trinuclear oxo-carboxylate complexes were also prepared by refluxing commercial chromium(III) nitrate salt with appropriate carboxylic acid. Reaction between chromium(III) nitrate and dichloroactetic acid yielded $[Cr_3O(Cl_2CHCOO)_6.3H_2O]NO_3.H_2O$ complex while combination of chromium(III) nitrate with trichloroacetic acid gave $[Cr_3O(Cl_3CCOO)_6.3H_2O]NO_3.2H_2O$. Besides, synthesis of chromium(III) acetate complex, $[Cr_3O(CH_3COO)_6.3H_2O]NO_3.7H_2O$ was also carried out by refluxing chromium(III) nitrate nonahydrate with glacier acetic acid. All the chromium(III) catalysts prepared are chemically and physically different from the starting materials. After synthesizing, the complexes were used in ethylene homopolymerization and copolymerization with propylene.

Chapter 2 describes the preparation and characterization of the chromium(III) trinuclear oxo-carboxylate complexes. The complexes were characterized using infrared spectroscopy (FTIR) and thermal analysis (TGA). Titrimetric method and TGA were used to determine the chromium content in each complex. The second part of chapter 2 describes the procedures of homo-polymerization of ethylene and propylene. Methods of characterization for the polymers were also reported.

Chapter 3 reported the synthesis results of chromium(III) complexes. The yield and the properties of each complex were described in details along with the spectra obtained from different charaterization tests. Chapter 4 reported the polymerization of ethylene using chromium(III) chloroacetate complex, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ in combination with diethylalumiun, $AlEt_2Cl$ as cocatalyst. The effect of various Al/Cr ratios and different polymerization temperature were investigated. Polymerization of ethylene was also carried out with the catalyst system being replaced by chromium(III) dichloroacetate, chomium(III) trichloroacetate and chromium(III) acetate complexes to study the effect of chloro- substituent groups on carboxylate ligand. The polymers obtained were characterized using FTIR and DSC. The last part of this chapter discussed propylene polymerization using chromium monochloroacetate-diethylaluminium catalyst system. The reason why it was incapable to obtain polypropylene yield was also discussed.

Chapter 5 describes the study of ethylene and propylene copolymerization. Chromium(III) chloroacetate complex, $[Cr_3O(ClCH_2COO)_6.3H_2O]NO_3.3H_2O$ in combination with $AlEt_2Cl$ were used as the catalyst in the polymerization reaction. Copolymer yield produced with different ethylene and propylene content was investigated. Effect of catalyst-cocatalyst aging time and various Al/Cr ratios were studied. FTIR and DSC methods were used to chracterized copolymers obtained.

Chapter 6 gave a conclusion on the works done and suggestion for future works.

References:

1. Nexant, *New Industry Outlooks for Polyethylene and Polypropylene,* 2008

2. A Guide to IUPAC Nomenclature of Organic Compounds, Blackwell Scientific Publications, Oxford, 1993

3. Kahovec, J., Fox, R. B. and Hatada, K. *Pure and Applied Chemistry* 2002, **74 (10),** 1921–1956

4. Boor, J. ‘Ziegler-Natta Catalysts and Polymerizations’, Academic Press, New York, 1979

5. Song et al. *Macromol. Symp.* 2004, **213**, 173-185

6. Mercandelli, P. et al. *Journal of Organometallic Chemistry* 2007, **692**, 4784–4791

7. Tamara Galloway, *Marine Pollution Bulletin*, 2008, 56(2), 163-165

8. Anon. *Chem. Eng*. 1970, **77**, 28

9. Count, A. D. ‘Catalysis- Volume 1 Specialist Periodical Reports’, The Chemical Society (ed), Billing & Sons Limited, London, 1976

10. Anon, *Hydrocarbon Processing* 1975, 188

11. WR Grace & Co. U. S. Patents 6,734,131. 2004

12. Sinn, H. and Kaminsky, W. *Ad.Organomet. Chem.* 1980, **18**, 99

13. Nur Diana Othman. ‘Structurally complex molybdenum oxide model catalysts from preparative nanoscience’, Kuala Lumpur: Universiti Malaya, 2004

14. Scheirs, John ‘Metallocene-based polyolefins : preparation, properties, and technology’, Wiley, Chichester, 2000

15. Benedikt, G. M. ‘Metallocene-catalyzed polymers : materials, properties, processing & markets’, Plastics Design Library, New York, 1998

16. Keii, T. ‘Kinetics of Ziegler-Natta Polymerization’, Kodansha Ltd, Tokyo, 1972

17. Jordan, D.O. *The Stereochemistry of Macromolecules*, Ketley A. D. (ed), 1967, **1**, 3

18. Ziegler, K., Holzkamp, E., Breil, H. and Martin, H. *Angew. Chem.* 1995, **67**, 541

19. Boor, J. *Macromol. Rev.* 1967, **2**, 115

20. Mandelkern, L. ‘Crystallization of Polymers’, McGraw-Hill New York – San Francisco – Toronto – London, 1964

21. Reich, L. and Schindler, A. ‘Polymerization by Organometallic Compounds’, Interscience Publishers, New York, 1966

22 Ziegler, K. *Bull. Soc. Chim.* France, 1956

23. Natta, G. *J. Poly. Sci.* 1995, **16**, 143

24. Natta, G. *Angrew. Chem.* 1956, **68**, 393

25. Natta, G. *Mod. Plastics* 1956, **34**, 169

26. Munoz-Escalona, A. and Prada, A. *Polymer*. 1979, **20**, 474-482

27. Zakharov, V. A., Bukatov, G.D., Chumaevskii, N. B. and Yermakov, Y. I. *Makromol. Chemie*. 1997, **178**. 967-980

28. Garoff, T., Jahamsson, S., Pesonen, K., Waldvogel, P. and Lindgren, D. *Eur. Poly. J.* 2002, **38**, 121-132

29. Zakharov, V. A., Makhtarulin, S. I., Perkovets, D. V., Moroz, E. M., Mikenas, T. B. and Bukatov, G. D. ‘Catalytic Polymerization of Olefins’, Keii, T. and Soga, K. (ed), Kodansha, Tokyo, 1985, 71-89

30. Lim, S. Y. and Choung, S. J. App. Cat. A: Gen. 1997, **153**, 103-118

31. Busico, V., Cipullo, R., Talarico, G., Segre, A. L. and Chadwick, J. C. *Macromolecules* 1997, **30**, 4786-4790

32. Nitta, K. H. and Tanaka, A. *Polymer* 2001, **42(3)**, 1219-1226

33. Ziegler, K. and Martin, H. *Makromol. Chem.* 1956, **186**, 18-19

34. Natta, G, Pino, P., Mazzanti, G. and Longi, P. *Gazz.* Chim. Ital., 1957, **87**, 549

35. Natta, G., Pino, P., Mazzanti, G. Ital. Pats. 535,712 (June 8, 1954), 537,425 (july 27, 1954), 526,101 (Dec. 3, 1954)

36. Natta, G., Pino, P., Mazzanti, G. and Longi, P. *Gazz.* Chim. Ital., 1957, **87**, 570

37. Ballard, D. G. H., Jones, E., Modinger, T. and Pioli, A. J. *Makromol. Chem.* 1973, *148*, 175

38. Natta,G., Pino, P., Mazzanti, G. U.S. Patents 3,000,870 Sept. 19, 1961, Montecatini; 2,992,212, July 11, 1961 E.H. DeButts, Hercules

39. McDaniel, M. P. and Welch, M. B. *Journal of Catalysis* 1983, **82**, 98

40. Alfred C. Battelle Memorial Institute, Ger. Offen. 2606243

41. Gan, S. N., Chen, S. I., Ohnishi, R and Soga, K., *Makromol. Chem. Rapid Commun*. 1984, **5**, 535

42. Gan, S. N., Chen, S. I., Ohnishi, R and Soga, K. *Polymer* 1987, **28**, 1391-1395

43. Gan, S. N., Lim M. C., Chen, S. I. and Soga, K. *J. Cat.* 1987, **105**. 249-253

44. Soga, K., Chen S. I., Doi, Y. and Shiono, T. *Macromolecules.* 1985, **19(12)**, 2893-2895

45. Carrick, W. L., Turbett, R. J., Karol, F. J., Karapinka, G.L., Fox, A. S. and Johnson R. N. *J. Poly. Sci: Part A-1* 1972, **10,** 2609-2620

46. Karol, F. J., Karapinka, G. L., Chi, S. W., Dow, A. W., Johnson, R. N. and Carrick, W. L. *J. Poly. Sci*: *Part A-1*. 1972, **10**, 2621-2621

47. Peucker, U. and Heitz, W. *Macromol. Rapid Commun.* 1997, **19,** 159-162

48. Yong, W.S., Uozumi, T., Terano, M. and Nitta, K. *Polyme*r. 2001, **42(23)**, 9644-9615

49. Britovsek, G. J., Gibson, V. C., Wass, D. F. *Angew. Chem.* 1999, Int. Ed. 38, 428

50. Bryliakov, K. P. *Russ. Chem. Rev*. 2007, **76**, 253

51. Semikolenova, N. V., Zakharov, V. A., Echevskaja, L. G., Matsko, M. A., Bryliakov,K. P. and Talsi, E. P. *Catalysis Today*, 2009, **144(3-4)**, 334-340

52. Natta, G. *J. Inorg. Nucl. Chem*. 1958, **8**, 589

53. Soga, K., Chen, S. I., Shiono, T. and Doi, Y. *Polymer*, 1985, **26**, 1888-1890

54. Aishah, M. J. ‘Synthesis of Some Chromium (III) Carboxylates and The Use of These Complexes as Ziegler-Natta Catalysts for the Polymerization of Ethylene’, Universiti Malaya, Kuala Lumpur, 1995

55. Friedlander, H. N. and Oita, K. *Ind. Eng. Chem.* 1957, **49**, 1885

56. Furukawa, J. and Tsuruta, T. *J. Polymer Sci.* 1959, **36**, 275

57. Natta, G. and Mazzanti, G. *Tetrahedron.* 1960, **8**. 86-100

58. Natta, G., Pino, P., Mazzanti, G., Giannini, U., Mantica, M. and Peraldo, M. *J. Polymer Sci.* 1957, **26**, 120

59. Patat, F. and Sinn,H. *Chim. Ind. (Milan)*, 1962, **44**, 474

60. Huggins, M. L. *J. Polymer Sci.* 1960, **48**, 473

61. Boor, J. *J. Polymer Sci.*, 1963, **C1**, 257

62. Cossee, P. *Tetrahedron Let.* 1960, **1(38)**, 12-16

63. Blais, P., Manley,R. J. St. *J.Polymer Sci. (A-1)* 1968, **6**, 291

64. Natta, G. *J. Poly. Sci: Nottingham Sym.* 1959, **14**, 21-48

65. Eirich, F. and Mark, H. F. *J. Colloid Sci.* 1960, **46**, 375

66. Saltman, W.M. *J.Polym. Sci.* 1960, **46**, 375

67. Schnecko, H., Reinmoller, M., Weirauch, K. and Kern, W. *J.Polym. Sci. (C)* 1964, **4**, 71

68. Keii, T., Soga, K. and Saiki, N. *J. Polym. Sci.* (C) 1967, **16**, 1507

69. Otto, F. D. and Parravano, G. *J.Polym. Sci. (A)* 1964, **2**. 5131

70. Burfield, D. R., McKenzie, I. D. and Tait, P. J. T. *Polymer* 1972, **13,** 302-306

71. Lukach, C. A. and Spurlin, H. M. ‘Copolymerization’, Ham, G.(ed), Wiley (Intersience), New York, 1964, 115

72. Natta, G. and Porri, L. ‘Polymer Chemistry of Synthetic Elastomers’ Kennedy, J. P. and Tőrnqvist, E. G. M. (ed.), Wiley (Intersience), New York, 1969, 23, 679-702

73. Cozewith, C.; Varstrate,G.; Ju, S. *Macromolecules* 1988, **21**, 3360-3370

74. Makino, K.; Tsuda, K.; Takaki, M. *Makromol Chem* 1992, **193**, 341-349

75. Kashiwa, N; Mizano, A.; Minami, S. *Polym Bull* 1984, **12**, 105

76. Dusseault, J. J. A.; Hsu, C. C. J. *Macromol Sci Rev Macromol Chem Phys C* 1993, **32**, 103-109

77. Alfrey, T. and Goldfinger, G. *The J. Chem. Phys.* 1944, **12(6),** 205-209

78. Odian, G. ‘Principles of Polymerization’, John Wiley & Sons, New York, 1991

79. Flory, P.J. ‘Principles of Polymers chemistry’, Cornell University Press, New York, 1953

80. Weinland, R. F. *Chem. Ber.* 1908, **41**, 3236

81. Chang, S. C., Jeffrey, G. A. *Acta Crystallogr. Sect. B*, 1970, **B26**, 673

82. Johnson, M. K., Powell, D. B. and Cannon, R. D. *Spectrochimica Acta* 1981, **37A(11)**, 995-1006

83. Earnshaw, A., Figgis, B. N. *J. Chem. Soc.*, 1966, **A**, 1956

84. Oh, S. M., Hendrickson, D. N., Hassett, K. L., Davis, R. E. *J. Am. Chem. Soc.* 1985, **107**, 8009

85. Cotton, F. A., Lewis, G. E. and Mott, G. N. *Inorg. Chem*, 1982, **21**, 3127

86. Nakamoto, K. ‘Infrared Spectra of Inorganic Coordination Compounds’, 2nd ed. Chapter 3, Wiley-Interscience, New York, 1987

87. Bellamy, L. J., ‘Advances in Infrared Group Frequencies’, Methuen & Co Ltd., London, 1968

88. Mansurov, M. M., Semonova, G. L., Yakubov, Kh. M. and Zhemchuzhnikova, T. A. *Russ. J. Inorg. Chem*. 1983, **28(6)**, 823-824

89. Bukovee, P. *Thermochim. Acta.* 1987, **110**, 383-387

90. Nikumbh, A. K., Rahman, M. M. and Aware, A. D. *Thermochim. Acta*. 1990, **159**, 109-123