

CHAPTER II

LITERATURE REVIEW

2.1 Background

Catalysis continues to play a vital role in polymerization of such olefins as ethylene and propylene. A voluminous patent and scientific literature describing transition metal catalysts for olefin polymerization have emerged since the original discoveries by Ziegler, Natta and other workers (Boor, 1979; Yermakov et al., 1981; Wilke, 1995 ; and Mulhaupt,1995). Significant progress in polymerization catalysis has been made in the last 30 years, particularly with the development of methods to increase the efficiency of transition metal catalysts in olefin polymerization. Success in this area has provided the basis of simplified, less costly, plant operation which does not require removal of residual catalyst from the polymer (Tait, 1979, 1989; Boor, 1979; Karol, 1984; Welch and Hsieh, 1993; and Mulhaupt, 1995)

Although much attention has been directed toward improvements in catalytic productivity, there has been, and continues to be, much active research on other important features of olefin polymerization. The specific nature of the catalyst has an important effect on molecular weight distribution, copolymerization kinetics, and degree of stereoregularity. Moreover, the size, shape, and porosity (morphology) of the catalyst particle plays an important role in regulating the morphology of the resulting polymer (Karol,1984; Floyd et al., 1986; and Forte et al.,1996). The innovations in polyolefin technology are schematically illustrated in Figure 2.1

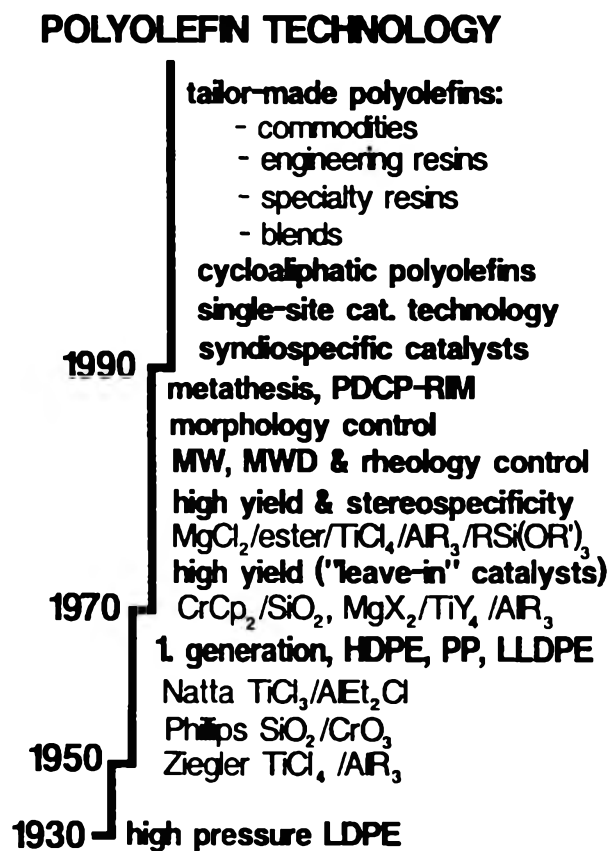


Figure 2.1 The innovations in polyolefin technology.

(Mulhaupt, 1995)

While significant technology advances based on new and improved catalysts have been made since the original discoveries, there is still widely held view that understanding of these catalysts is meager and empirical. It is true that olefin catalytic processes are not generally understood in the detailed mechanistic sense. Certain general requirements have been identified to be critical in this polymerization. This chapter reviews segments of current catalyst research activities in olefin polymerization and current perspectives in these research areas.

2.2 Titanium-Aluminum Alkyl Catalysts

In the early 1950s, transition metal catalyzed olefin polymerization started with work done both in the United State and in Europe ; see Table 2.1.

For titanium-aluminum alkyl catalysts, initially the use of these catalysts to produce polyethylene grew at a much slower pace than the chromium oxide on silica catalysts. The main difficulty with the original catalysts was the yield of polymer per unit of catalyst in low pressure processes was so low that the catalyst residue in the polymer had to be extracted. Typical yields of some of these early catalysts were under 5 kg of polyethylene per gram of transition metal, which resulted in titanium residuals as high as 100 ppm. Not only were titanium residuals high but also chloride levels were correspondingly high, resulting in severe corrosion problems in addition to color and stability problems caused by the metal residue. The only way to avoid these problems was to remove these entities from the polymer by using expensive wash columns. However, research on these catalysts to improve activities continued at a rapid pace. In the end these efforts were very successful, and the market place today is supplied with the sought-after

Table 2.1 Early discoveries of low pressure linear polyethylene
(Welch and Hsieh, 1993)

| Research group | Catalysts | Time of initial discovery | Early polymer density (g/cm ³) |
|---|---|---------------------------|--|
| Alex Zletz, Standard Oil of Indiana | Nickel oxide on activated carbon Molybdenum oxide on alumina | Early 1950 | 0.96 |
| J. Paul Hogan and Robert L. Banks, Phillips Petroleum Co. | Chromium oxide on silica alumina | 1951 | 0.95–0.97 |
| Karl Ziegler et al., Max Planck Institute for Coal Research | TiCl ₄ + R ₃ Al | Late 1953 | 0.945 |

Table 2.2 Early supported catalysts
(Welch and Hsieh, 1993)

| Patent no. | Date | Company | Catalyst preparation |
|----------------|------|------------------------|---|
| BP 841,822 | 1955 | British Petrochemicals | TiCl ₄ reduced by aluminum alkyls in the presence of solids such as MgCO ₃ |
| U.S. 3,153,634 | 1956 | Sun Oil | TiCl ₄ was adsorbed on SiO ₂ /Al ₂ O ₃ and reduced |
| U.S. 2,980,662 | 1956 | Sun Oil | Ti compounds reduced in the presence of solid NaCl, FeCl ₃ , AlCl ₃ , GaCl ₃ , etc. |
| BP 877,457 | 1957 | Sun Oil | TiCl ₄ reduced in the presence of inorganic compounds |
| BP 969,761 | 1960 | Cabot | Transition metal compounds reduced in the presence of SiO ₂ , Al ₂ O ₃ , SiO ₂ /Al ₂ O ₃ , ZrO ₂ , TiO ₂ , ThO, MgO, etc. |
| BP 969,767 | 1963 | Cabot | Transition metal compounds reduced in the presence of SiO ₂ , Al ₂ O ₃ , SiO ₂ /Al ₂ O ₃ , ZrO ₂ , TiO ₂ , ThO, MgO, etc. |

titanium-aluminum alkyl produced resin from processes (slurry, solution, and gas phase), which are much more economical than the earlier versions.

The advance in titanium-aluminum alkyl catalysts resulted from efforts to form supported catalysts on a variety of materials. Table 2.2 shows some of the initial work on supported early transition metal catalysts. The first supports were metal oxides, halides, and carbonates. Although they did not accomplish the goal of eliminating catalyst removal process steps, they did point the direction and provide the needed incentive to continue the efforts.

In the mid-1960s the work on these transition metal supported systems began to reach fruition. A series of patents dealing with supporting halo-titanium species on hydroxymagnesium halides came out (Table 2.3). The degree of dehydration of the support played a significant role in their activities. The small average particle size and relatively high specific surface areas also helped to produce optimum results. While the classic supported catalyst approach used transition metals attached to surface hydroxy species, other groups were finding the transition metal did not have to be anchored to the support for high activities. Many of these catalysts (Table 2.4) consisted of magnesium alkoxides reacted with transition metal halides. By the end of the 1960s, there was a good deal of interest in this new type of catalyst, which no longer required expensive deashing steps.

Gradually evolving from all this concentrated titanium-aluminum alkyl catalysts research was even higher activity catalysts. These supported approaches eventually led to catalyst systems consisting of MgCl_2 ball-milled with TiCl_4 which could polymerize propylene with a high yield [>50 kg PP/g Ti] and good stereospecificity [isotactic index $> 90\%$]. The results by the early 1970s were yet another boost in catalyst activity, which was at this point high enough to eliminate all deashing steps (Table 2.5).

Table 2.3 Magnesium hydroxychloride supported catalysts
(Welch and Hsieh, 1993)

| Patent no. | Date | Company | Catalyst preparation |
|----------------|------|----------------|---|
| BP 1,024,336 | 1963 | Solvay | Reaction of a transition metal compound with a hydroxychloride of a bivalent metal, preferably Mg(OH)Cl |
| JP45-40295 | 1967 | Mitsui | TiCl ₄ reacted with Mg(OH) ₂ and reduced |
| U.S. 3,634,384 | 1968 | B. F. Goodrich | TiCl ₄ reacted with Mg(OH) ₂ and reduced |
| BE 726,839 | 1968 | Solvay | Reaction of magnesium hydroxide with a transition metal halide. |
| BE 728,002 | 1968 | Montecatini | |
| BE 735,291 | 1968 | Hoechst | |

Table 2.4 Magnesium alkoxide based catalysts
(Welch and Hsieh, 1993)

| Patent no. | Date | Company | Catalyst preparation |
|----------------|------|---------|--|
| U.S. 3,644,318 | 1968 | Hoechst | TiCl ₄ reacted with Mg(OR) ₂ or a complex magnesium alkoxide |
| BE 758,994 | 1969 | Hoechst | |
| BE 743,325 | 1969 | Solvay | |
| BE 780,530 | 1971 | Hoechst | Reaction of magnesium alkoxide and an acid halide with a tetravalent titanium compound |
| NL 216,195 | 1971 | Solvay | |

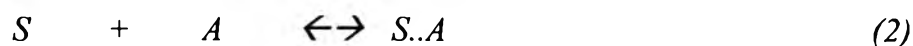
Table 2.5 Magnesium chloride based catalysts
(Welch and Hsieh, 1993)

| Patent no. | Date | Company | Catalyst preparation |
|----------------|------|-------------|---|
| BP 1,286,867 | 1968 | Montecatini | TiCl ₄ ball-milled with MgCl ₂ |
| BE 744,221 | 1969 | Montecatini | Reaction of MgCl ₂ with halogenated titanium compounds |
| BE 747,846 | 1969 | Montecatini | |
| JP 46-34092 | 1968 | Mitsui | TiCl ₄ reacted with MgCl ₂ · nROH or MgCl ₂ · nH ₂ O or MgCl ₂ · Lewis base |
| U.S. 3,642,746 | 1968 | Mitsui | |
| JP 46-34093 | 1968 | Mitsui | |
| BE 755,185 | 1969 | Hoechst | Reaction of a magnesium dihalide electron donor adduct (e.g., MgCl ₂ · 6C ₂ H ₅ OH) with a titanium compound |

Many of the requirements necessary for the economic production of polyethylene and polypropylene have been partially achieved. However, catalysts of greater activity and of greater selectivity in the production of polymers and copolymers for specialty applications can be anticipated.

2.3 Effect of Cocatalyst

The concentration of alkylaluminium affected the kinetic rate-time profiles as shown in Figure 2.2. The polymerization rate as a function of Al/Ti ratio showed a maximum (Keii, 1986; Kim et al., 1990; Jaber and Ray, 1993; Marques et al., 1993; Chareonsuk, 1995) at Al/Ti *c.a.* 50, as shown in Figure 2.3, Marques et al. (1993) concluded that at this maximum the active centers are formed completely, or the maximum equilibrium value of active center has been reached. The initial increase in rate with increase in Al/Ti is believed to be due to the continuation of active site formation (Munoz-Escalona et al., 1984; Zakharov et al., 1986). The decrease in rate with further increase in Al/Ti after reaching the maximum rate is believed to be due to progressive over-reduction of titanium (Boor, 1979; Riechert, 1983). Another possible explanation for the decrease in rate is competitive adsorption between triethylaluminium cocatalyst and ethylene monomer on the same site (Kim et al., 1990; Tiat et al., 1990). A Langmuir-Hinshelwood rate equation which applies to this mechanism is



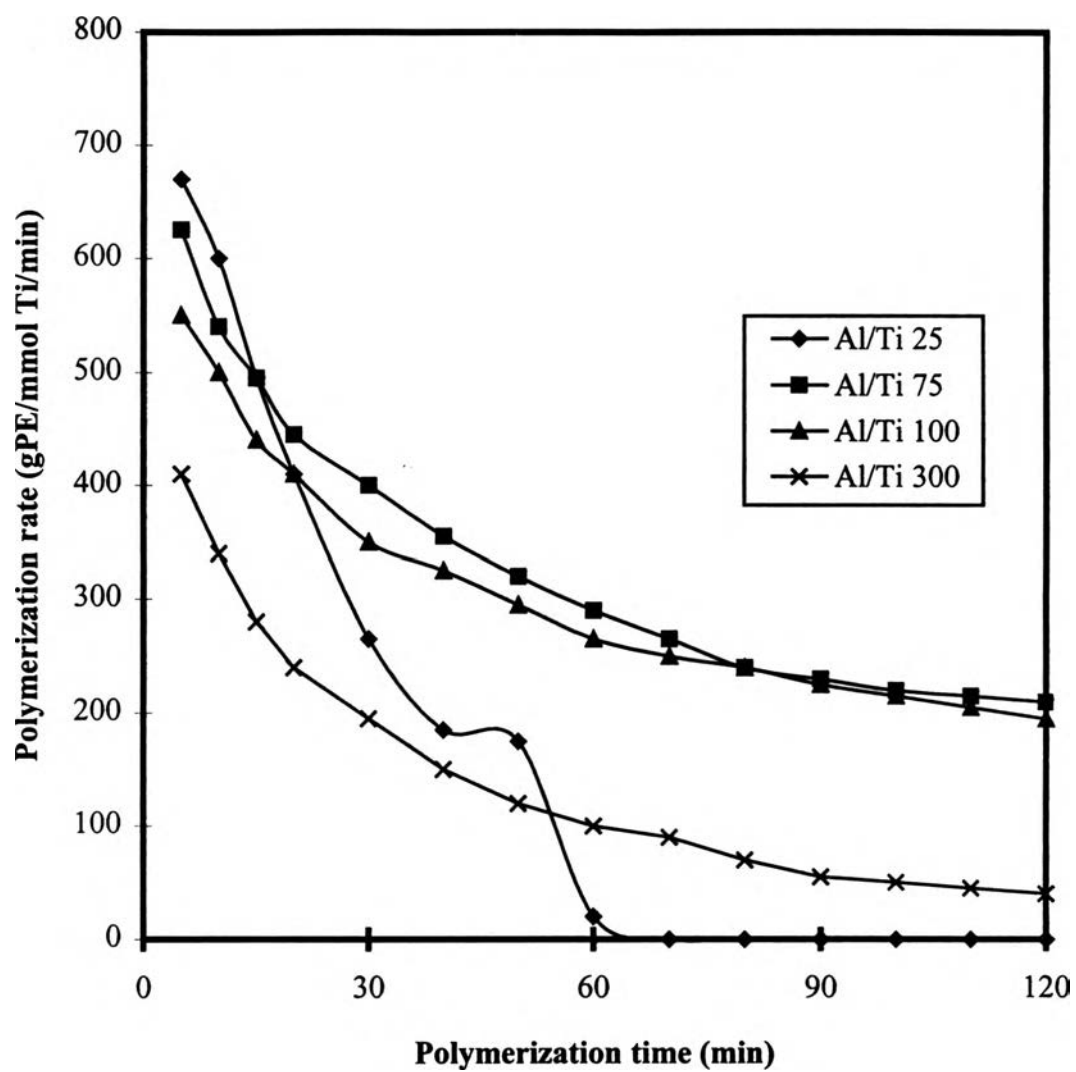


Figure 2.2 Effect of Al/Ti ratio on polymerization rate.

(Chareonsuk, 1995)

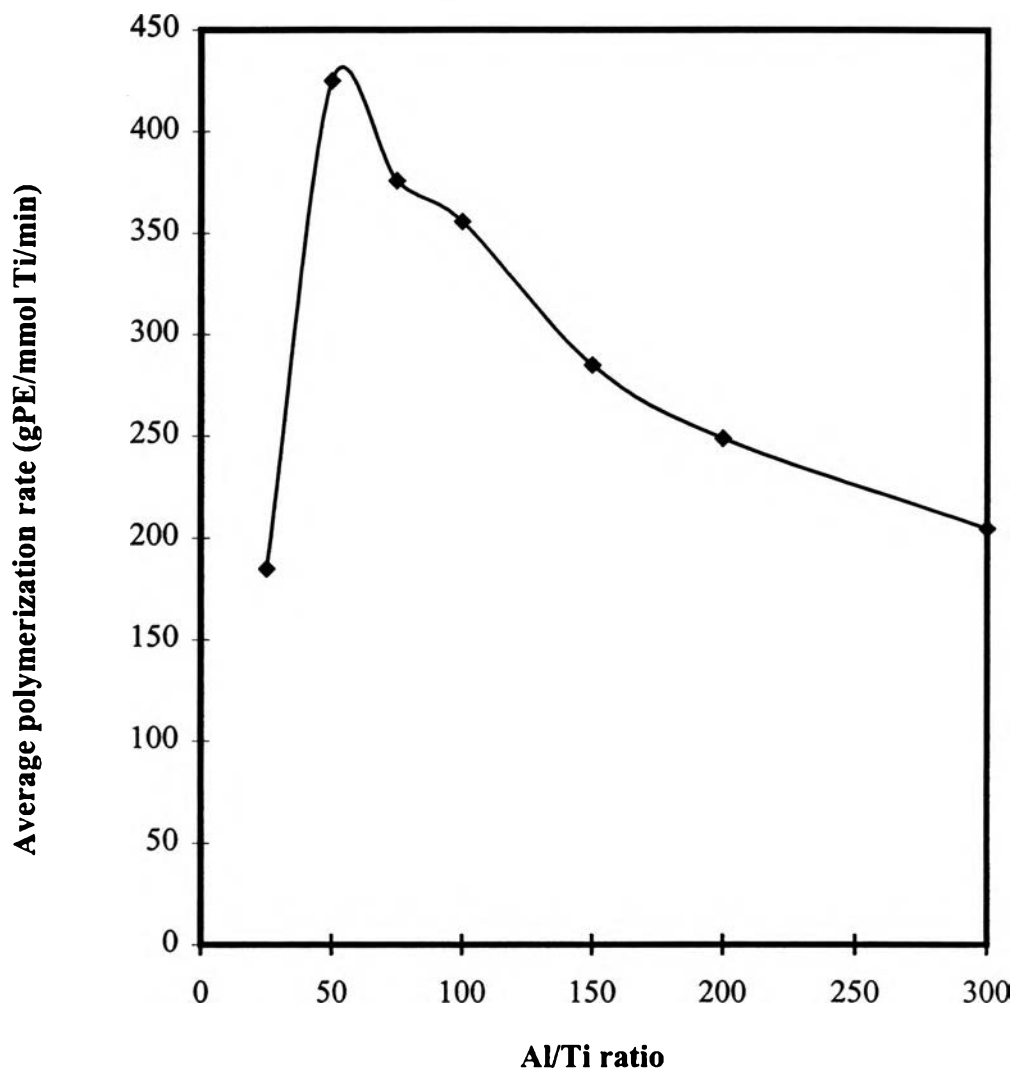


Figure 2.3 Dependence of polymerization rate on Al/Ti ratio.
(Chareonsuk, 1995)

The rate of polymerization is given by

(Note: the notations are defined in the appendix)

$$R_p = k_p C^* \theta_A \theta_M \quad (3)$$

Hence

$$R_p = \frac{k_p C^* K_A K_M [M][A]}{(1 + K_M [M] + K_A [A])^2} \quad (4)$$

Under condition in which [M] is constant and if $K_A \gg K_M$, this can be written as:

$$R_p = \frac{k'' C^* K_A [A]}{(1 + K_A [A])^2} \quad (5)$$

Since k'' is almost constant, an increase in the K_A value might be one reason for the polymerization rate decrease with polymerization time because the alkylaluminium is adsorbed more strongly than monomer.

2.4 Effect of Temperature

Polymerization temperature has an effect on polymerization rate showing a maximum (Floyd et al., 1986; Kim et al., 1990; Jaber and Ray, 1993; Chareonsuk, 1995). As shown in Figure 2.4, the polymerization rate.

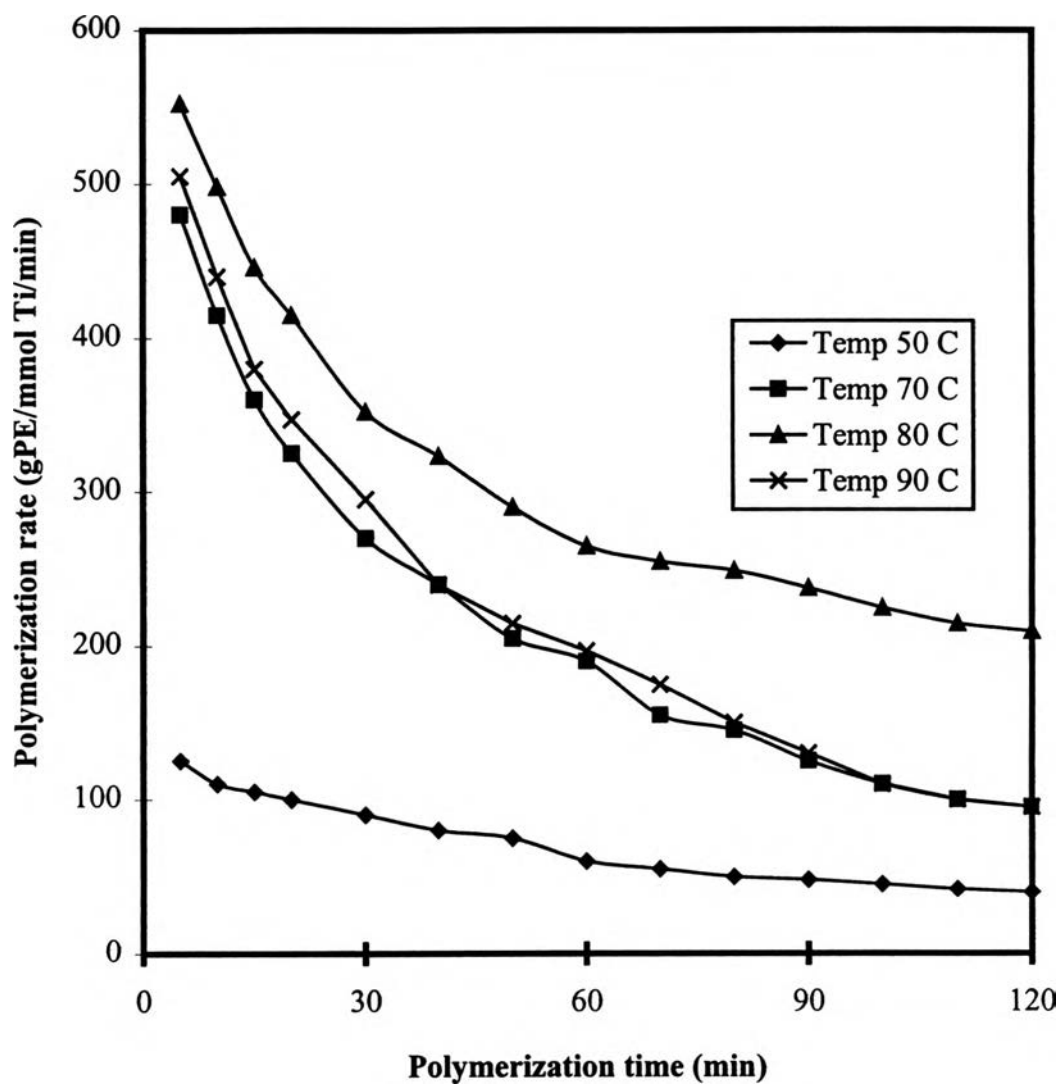


Figure 2.4 Effect of temperature on polymerization rate.

(Chareonsuk, 1995)

increased as temperature increased from 50 to 80 °C. Then decreased above 80 °C. The increase in polymerization rate is proportional to the polymerization temperature, indicating that the rate of active site formation is greatly dependent on polymerization temperature. The drastic decrease in the rate at temperature above 80 °C is believed to be due to the destruction of active sites (Jaber and Ray, 1993; Chareonsuk, 1995).

From the Arrhenius equation (Fogler, 1992) :

$$k_p = A e^{-E/RT} \quad (6)$$

and the polymerization rate law (Keii, 1986) :

$$R_p = k_p C^* [M] \quad (7)$$

at constant C^* , substitute equation (6) in equation (7) and rearrange,

$$R_p / [M] = A e^{-E/RT} \quad (8)$$

Generally, overall activation energy values in the range of 9-11 kcal/mole have been observed for polymerization of ethylene with the $TiCl_4/MgCl_2$ catalytic system (Marques et al., 1993; Chareonsuk, 1995).

2.5 Mechanisms of Polymerization

It is generally accepted that chain growth occurs by the monomer insertion into the transition metal-carbon bond, although the detailed structure

of the active center is still poorly understood. The most widely accepted mechanism involving chain growth at the transition metal alkyl is that devised by Cossee (1961). He proposed an active center model based on a titanium atom having an octahedral configuration surrounded by four chlorine ligands from the crystal lattice, an alkyl group introduced by the activator and a coordination vacancy (Figure 2.5).

Polymerization occurs *via* complexation of an alkene molecule at the coordination vacancy followed by transfer of the alkyl group to the bound alkene. A new σ -bond is formed between the growing polymer and the transition metal atom. The new structure formed is equivalent to the original except that the positions of the alkyl group and vacancy have exchanged as shown in Figure 2.6.

Cossee provided strong support for this mechanism from molecular orbital calculations. Figure 2.7 shows the overlap of the molecular orbitals which are involved in the formation of a π -bond between the alkene and the transition metal.

The metal-alkyl bond of the $\text{RTiCl}_4\text{---}\square$ complex is stable in the uncomplexed state. However, coordination of an alkene molecule results in a mixing of d orbitals from the metal with π^* antibonding orbitals from the alkene. The resultant orbital is sufficiently lower in energy relative to the original metal $3d$ orbitals that an electron can easily be excited into it from the metal-alkyl bond. The resultant metal-alkyl attaches itself in a concerted way to the nearest carbon atom of the bound alkene.

The mechanism of Rodriguez and Van Looy (1966) has features of the Cossee model, as well as the bimetallic models proposed by Natta (1960). The nature of the metal-alkyl determines the stereoregularity of the polymer formed due to steric interaction with the complexed alkene (Figure 2.8).

In summary, the concept of polymerization propagation occurring at the transition metal-alkyl bond has been generally accepted. The mechanism of Cossee together with its subsequent modifications has been widely adopted.

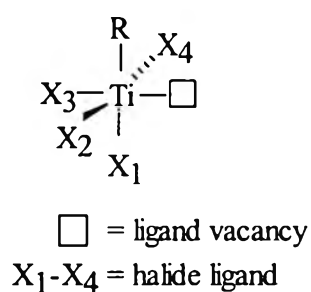


Figure 2.5 Titanium atom having an octahedral configuration.

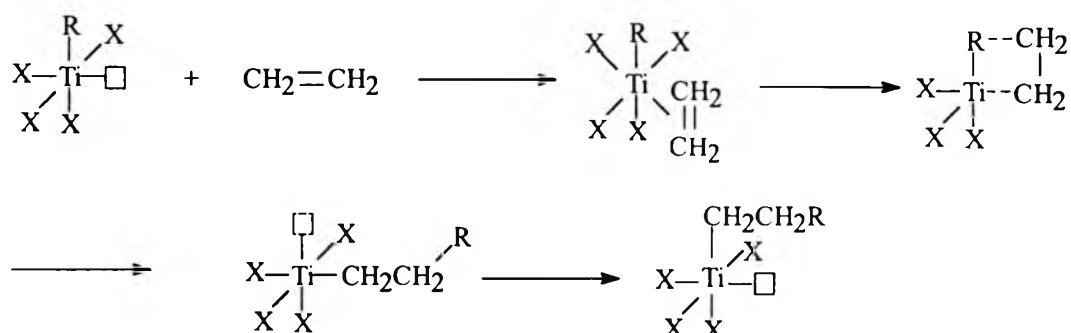


Figure 2.6 Proposed mechanism by Cossee (1961).

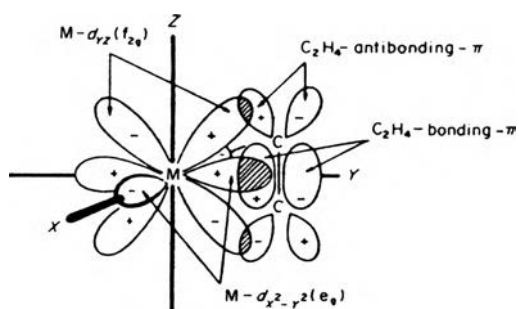


Figure 2.7 Molecular orbital overlap in the Cossee mechanism .

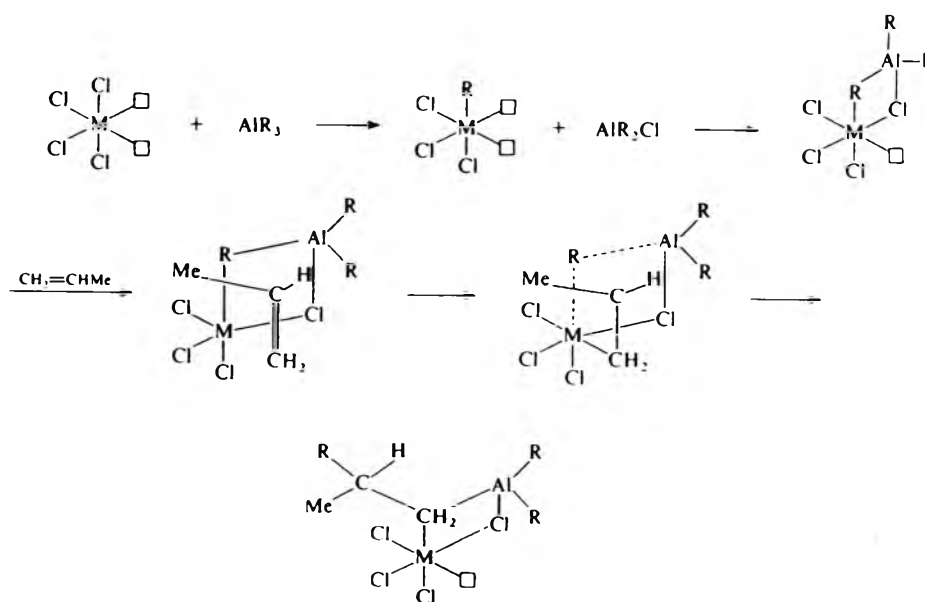


Figure 2.8 Proposed mechanism by Rodriguez and Van Looy (1966).

2.6 Activation of Dead Centers by Chlorinated Compounds

Under the conditions of polymerization the active centers undergo reduction to a lower valence state metal species that are no longer active for polymerization of the olefin. The third component oxidizes this inactive species to a higher valence state compound which is easily realkylated to form an active center.

Halogenated organic molecules have been found to be very efficient activators (promoters) in vanadium base catalysts. Beran et al. (1984), Zoeckler et al. (1988) and Kao et al. (1991^a,1991^b) found extremely high polymerization rates for ethylene when chloroform (CHCl_3) was added to the supported vanadium (VCl_4) catalyst in an ethylene polymerization. Kao et al. (1991^a,1991^b) also found that the polyethylene produced is narrower molecular weight distribution. Adisson et al. (1994) and Rebeiro et al. (1995) found that various types of chlorine containing activators (such as CCl_4 , CHCl_3 and CH_3CCl_3) strongly increased the productivity of the supported vanadium catalyst ($\text{VCl}_3/\text{AlCl}_3$) and the intensity of the activating effect was found to depend on the nature of the activator used, the most effective one being CH_3CCl_3 .

Activations of titanium based catalysts by chloroalkanes were observed by other workers. Fushman et al. (1965) found the activities of the $(\text{C}_5\text{H}_5)_2\text{TiCl}-\text{Al}(\text{C}_2\text{H}_5)\text{Cl}$ and $(\text{C}_5\text{H}_5)_2\text{TiCl}-\text{Al}(\text{C}_2\text{H}_5)\text{Cl}_2$ catalysts were greater in the presence of the chlorinated compounds and showed that the oxidation of Ti(III) to Ti(IV) had occurred.