CHAPTER II
LITERATURE SURVEY

2.1 Synthesis and Structure of Catalyst

Transition metal compounds of group IV to VIII (e.g., $TiCl_4$) mixed with a metal alkyl of base metal of group I to IV (or alkylaluminum e.g., $Al(C_2H_4)_3$) results in active centers of Ziegler-Natta catalysts and readily polymerizes various olefins and dienes. Neither of the principal catalyst component, if used alone, can polymerize alkenes.

Magnesium chloride ($MgCl_2$) is widely used as a support. $MgCl_2$-supported transition metal catalysts are prepared either by ball milling $MgCl_2$ with a transition metal compound or by simply chemically reacting these compounds. Dusseault et al. (1993) suggested that $MgCl_2$ can increase the catalyst activity because of a more efficient dispersant of active titanium on the surface. Moreover, $MgCl_2$ support also affected the electronic nature of the titanium in such a way as to enhance polymerization activity. Soga et al. (1984) explained that $MgCl_2$ back-donates electrons to the more electronegative titanium, which in turn stabilizes coordination of monomers. The result is an acceleration of monomer insertion.

The alkylaluminum (sometimes called co-catalyst) activitates the polymerization reaction in two ways. First, it reduces Ti^{4+} to Ti^{3+} as suggested by Kashiwa et al. (1984). Then the alkylaluminum alkylates the Ti^{3+} as investigated by Chien et al. (1985). The activation process is shown in Figure 2.1.
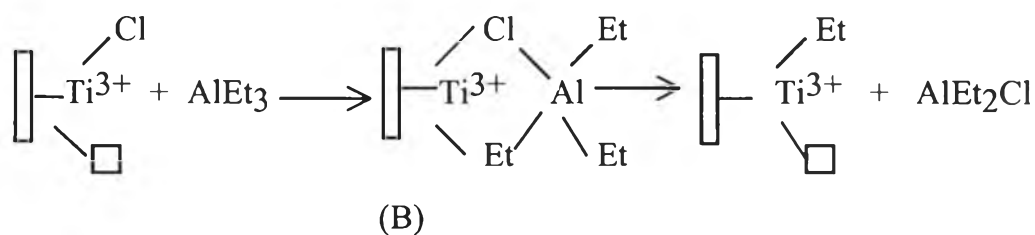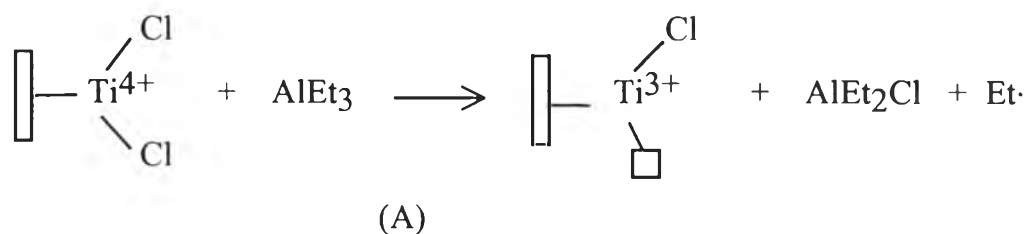
$$\big[\!-\!\mathrm{Ti}^{4+}\big\langle{}^{Cl}_{Cl} \quad + \quad AlEt_3 \quad \longrightarrow \quad \big[\!-\!\mathrm{Ti}^{3+}\big\langle{}^{Cl}_{\square} \quad + \quad AlEt_2Cl \quad + \quad Et\cdot$$

(A)

$$\big[\!-\!\mathrm{Ti}^{3+}\big\langle{}^{Cl}_{\square} + AlEt_3 \longrightarrow \big[\!-\!\mathrm{Ti}^{3+}\big\langle{}^{Cl}_{Et}\big\rangle Al\big\langle{}^{Et}_{Et} \longrightarrow \big[\!-\!\mathrm{Ti}^{3+}\big\langle{}^{Et}_{\square} + AlEt_2Cl$$

(B)

Figure 2.1 The activation process: (A) reduction of $TiCl_4$ as proposed by Kashiwa et al. (1984); (B) alkylation reaction proposed by Chien et al. (1985).

Typically, the alkylaluminum is used in excess of a stoichiometic ratio with respect to molar concentration of active titanium centers because it also acts as a scavenger of impurities.

2.2 Physicochemical Phenomena

The $MgCl_2$-supported catalytic polymerization reactions are considered to be heterogeneously catalyzed reactions. So it is important to study the diffusional mass transfer and heat removal effects on the reaction. Floyd et al. (1986) studied these effects on the rate of polymerization by using the multigrain model shown schematically in Figure 2.2. This model structure is based on numerous experimental observations that the original catalyst particle

quickly breaks up into many small catalyst fragments which are dispersed throughout the growing polymer. Thus, the large macroparticle is comprised of many small polymer particles (microparticles), which encapsulate these catalyst fragments.
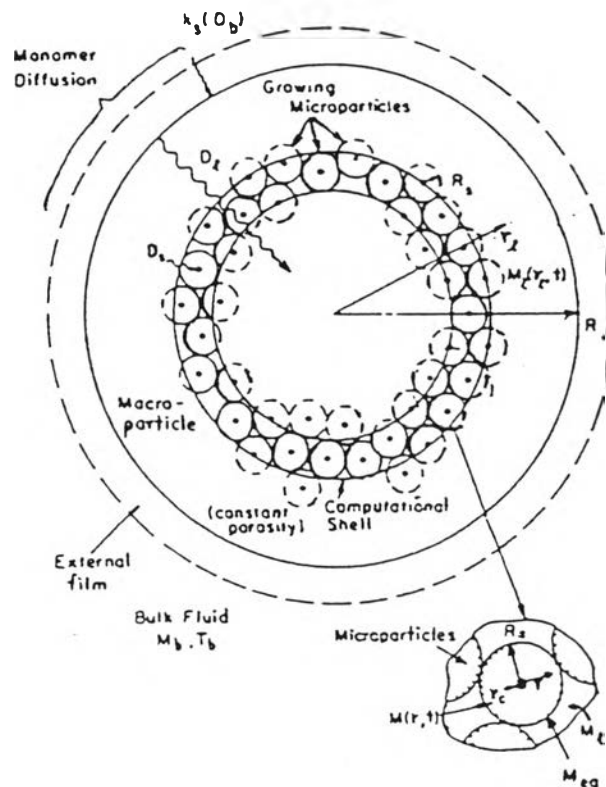

Figure 2.2   The multigrain model (Floyd et al., 1986).

Follestad (1996) has developed a two-phase (pore phase and polymer phase) transport theory which explains that the polymer particles are porous and mass transfer takes place not only in the polymer phase but also in the pore phase (liquid or gas), both in series in these two phases as well as in parallel. This model is shown in Figure 2.3.
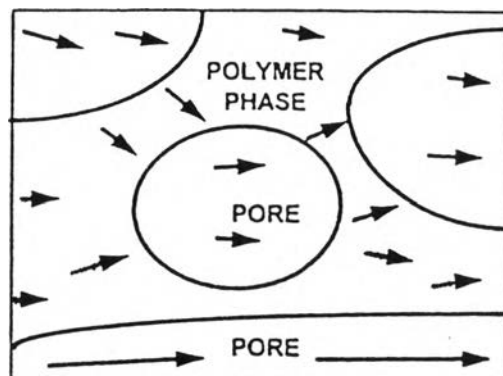
Figure 2.3   Principle of two-phase transport theory (parallel and series) (Follestad, 1996).

2.3   Mechanism and Kinetics of Polymerization

Although it has not been proven quantitatively, the mechanism proposed by Cossee (1964) seems to be the best representation of what is happening at the active center (Figure 2.4). The titanium atom is in an octahedral coordination environment with one site vacant and adjacent coordination site bonded to an alkyl group (polymer chain). For supported catalysts this structure is created when bound $TiCl_4$ reacts with alkylaluminum to form the active site as discussed earlier.

The two-step mechanism for propagation involves π-coordination of an incoming monomer by the titanium atom at its vacant coordination site, followed by insertion , via a four-center transition state, into the titanium-alkyl (polymer) bond. Then the growing polymer chain migrates back to it original position after each insertion in order to maintain sterically identical propagation steps. However, the rate determining step is still unclear because

the propagation rate constants are obtained by estimating the concentration of active sites (Dusseault et al., 1993).
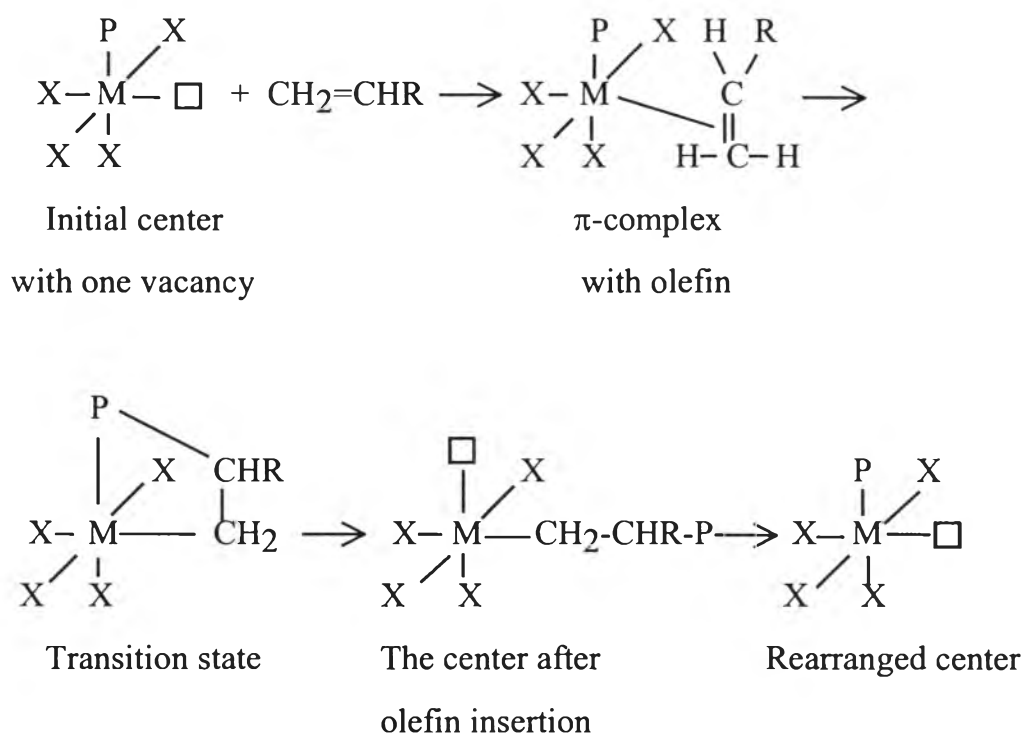

Figure 2.4 The Cossee mechanism (Cossee, 1964).

Generally, the polymerization rate of $MgCl_2$-supported Ziegler-Natta catalyst is initially high, followed by a rapid decay to a near stationary rate. A first order dependence on monomer was displayed over the typical range of monomer concentrations seen in slurry reactors (Marques et al., 1993; Chareonsuk, 1995). Adsorption isotherm theory is used to describe the kinetic behavior. Chareonsuk (1995) used the Langmuir-Hinshelwood mechanism to explain the dependence of polymerization rate on the monomer concentration and triethylaluminum concentration. The rate expression is shown below:

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

where R_p = the polymerization rate;

k_p = the propagation rate constant;

K_A = adsorption equilibium constant for monomer;

[M] = the monomer concentration in a polymer-solution system;

[A] = alkylaluminum concentration;

C^* = the active site concentration.

Marques et al. (1993) suggested that the decay in rate of polymerization with time could be represented by a first order decay law.

2.4 Dependence of Polyethylene Properties and Polymerization Conditions

The most important properties of polyethylene are molecular weight and polydispersity (or molecular weight distribution). Hydrogen is commonly used as a chain transfer agent to control molecular weight of polyethylene. Sripruitkiat (1995) reported that higher partial pressures of hydrogen and higher polymerization temperatures could lower the molecular weight of polyethylene. Choi et al. (1997) developed a computer simulation using a kinetic model to predict the molecular weight of polyethylene produced in a semibatch slurry reactor.

The polydispersity of polyethylene produced by heterogeneous Ziegler-Natta catalysts is typically in the range of 3-10 (Dusseault et al., 1993). Doi et

al. (1981) suggested that diffusion was a source of broad molecular weight distribution. However the existence of the broad molecular weight distribution in the absence of diffusion control at the active site has led to the general acceptance that the catalyst has active sites of varying activity. This was supported by a nonlinear decrease in polymerization rate with loss of active centers (due to CO poisoning) observed by Doi et al. (1981).

2.5 Low Molecular Weight Polyethylene

There are few research studies of the low molecular weight polyethylene. Generally, polyethylene produced from $MgCl_2$-supported Ziegler-Natta has a broad molecular weight distribution (BMWD). This BMWD characteristics will generate a low molecular weight polyethylene fraction or by-product in the higher amount than narrow molecular weight distribution (NMWD). However, the amount of low molecular weight polyethylene produced also depends on the polymerization conditions. Metallocenes can be used to reduce the amount of low molecular weight polyethylene produced. Speca et al. (1997) suggested that the broad molecular weight distribution (BMWD) polyethylene produced from mixed metallocenes lacks low molecular weight polyethylene found in BMWD polyethylene produced from $MgCl_2$-supported Ziegler-Natta catalysts or conventional catalysts.

To utilize this by-product, Munteanu et al. (1994) studied controlled oxidation of low molecular weight polyethylene. The product from this process can be used in many applications such as additives for plastics and organic coatings, PVC lubicants, etc.