

CHAPTER III

EXPERIMENTAL SECTION

3.1 Scope of Research Work

To develop the Ziegler-Natta catalytic system for polyethylene synthesis by studying the effect of the following conditions

- Types of chlorinated compound
- Concentrations of chlorinated compound

On the activity and productivity of the polymerization

3.2 Experimental Plans

3.2.1 Fixed or controlled parameters

- Catalyst concentration ($Ti = 0.01 \text{ mmol/l}$)
- Amount of cocatalyst ($Al/Ti = 100$)
- Temperature ($T = 80 \text{ }^\circ\text{C}$)
- Partial pressure of ethylene ($P_{C_2} = 4.5 \text{ kg/cm}^2$)
- Partial pressure of hydrogen ($P_{H_2} = 2.5 \text{ kg/cm}^2$)
- Total pressure ($P_t = 8.0 \text{ kg/cm}^2$)

3.2.2 Variable parameters

- Types of activator ($CHCl_3$, CH_3CCl_3 , and $C_6H_5CH_2Cl$)
- Amount of activator ($Act/Ti = 0-1$)

3.3 Materials

Ethylene: The gas supplied by National Petrochemical (Public) Company was dried over molecular sieves (3 Å).

n-Hexane: Commercial solvent supplied by Shell Chemicals (Public) Company was fractionally distilled.

Butene-1: The gas supplied by Bangkok Synthetic (Public) Company was purified over molecular sieve (13X).

Hydrogen: The gas supplied by National Petrochemical (Public) Company was purified by Pressure Swing Adsorption.

Nitrogen: The gas was supplied by Bangkok Industrial Gas (Public) Company was used as received.

Triethylaluminium: This alkyl supplied by Nippon Alkyls Company was used as received.

Supported titanium catalyst: A high activity magnesium chloride-supported titanium halide catalyst was used for this thesis.

Chlorinated compound: Three types of chlorine containing activators; CHCl_3 , CH_2Cl_2 , and $\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$ were used.

3.4 Catalyst Preparation

The catalysts were prepared according to the preparation procedure described below. (Chien, 1984; Karol, 1984)

The entire catalyst preparation was carried out in an oxygen-free and moisture-free environment using the Sclenck apparatus. Transfers were made in a dry box. Anhydrous MgCl_2 was large silvery flakes. It was heated for 30 min at 380 °C under a stream of HCl; 8 ml of H_2O was collected from 73g of MgCl_2 . The temperature was increased to 430 °C under an argon atmosphere, followed by vacuum drying for 5 h to give **Support I**.

To 33.5 g of Support I was added 7.8 ml of ethyl benzoate (EB) in a molar ratio of 1 MgCl_2 :0.155 EB and ball-milled with cylindrical porcelain elements. The resulting product, after thorough washing with hexane and drying, is referred to as **Support II**.

To 2.7 g of Support II was suspended in hexane, and 1.5 ml of p-cresol (PC) ($\text{MgCl}_2/\text{EB}:\text{PC}=1:0.5$) was added dropwise over a 1 h period with stirring at ambient temperature. The reaction mixture was heated to 50 °C for 1 h and subsequently washed and dried to give **Support III**.

To 21 g of Support III was added 5.2 ml of Triethylaluminium (TEA) which corresponds to a PC:TEA molar ratio of 2:1. The mixture was stirred for 1 h at room temperature, filtered, washed and dried under vacuum to give **Support IV**. During the course of reaction, the evolved gas was quantitatively collected and determined to be ethane by mass spectrometry. One mole of C_2H_6 was liberated from 1 mol of PC in the Support.

The final process is the reaction of 1.55 g of Support IV in 5 ml of hexane with 10 ml of TiCl_4 at 100 °C followed by thorough washing to form the “Catalyst.”

3.5 Analysis of Total Titanium Content

The total Ti in the catalyst and the complexes of TiCl_4 was determined using the colorimetric method (Vogel, 1950). A known amount of catalyst was dissolved to 10 ml of concentrated sulfuric acid and 10 ml of 3% H_2O_2 . The solution was dilute to 100 ml with distilled water. The UV-VIS absorbance of the solution at 410 nm was measured with a Philips 8700 spectrophotometer. The wt % of Ti was then calculated from a calibration curve derived from the absorbance measurements of standard Ti solutions.

3.6 Reactor System

The following apparatus was set up with instruments as the reactor system for polymerization (Chareonsuk,1995). The schematic diagram is shown as Figure 3.1.

1. A 2-litre jacketed stainless steel autoclave of Buchi A.G., model BEP 280 equipped with variable speed motor and anchor-type agitator.
2. Mass flow meter of Omega Engineering, inc., model FMA-5610-st. Range 0-20 Standard liters per minute.
3. A temperature controller of Matsui, model MCO-15H.

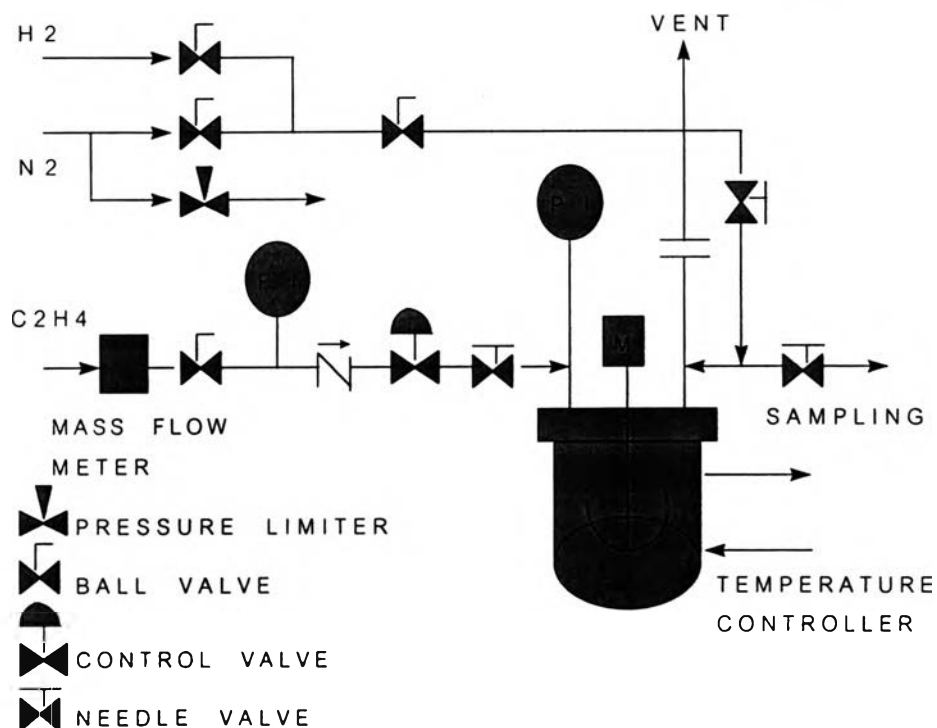


Figure 3.1 The schematic diagram of polymerization reactor system.

3.7 Polymerization Procedure

The ethylene polymerization was carried out in a stainless steel jacketed reactor. The reactor was purged and dried by N_2 at $80\text{ }^\circ\text{C}$ for 1 h and cooled down to $40\text{ }^\circ\text{C}$. The solvent, hexane, was bubbled with dried N_2 for 1 h before being added to the reactor. Cocatalyst and catalyst were introduced by means of a pipette under dried N_2 . In the case of activator addition, the activator was introduced by mean of a pipette under dried N_2 as well.

The reactor was then heated to $80\text{ }^\circ\text{C}$. The temperature was controlled by a thermostatic water bath. H_2 and C_2H_4 were then fed into the reactor for partial pressure of 2.5 bar and 4.5 bar respectively. The reaction started

immediately. Only C_2H_4 was automatically fed through a pressure control valve to maintain a total pressure of 8 bar. The flow rate of ethylene consuming was measured by mass flow meter.

The polymerization was performed for 2 h. The polymerization time, temperature and C_2H_4 flow rate were monitored and recorded.

After 2 h, the reactor was cooled down and purged with N_2 to ambient temperature and pressure. The hexane/polyethylene slurry was filtered and polyethylene was then dried in a vacuum oven at 100 °C for overnight. Finally, the polyethylene powder was weighed.

3.8 Polymer Characterization

Gel Permeation Chromatography (GPC) was used to determine molecular weight distributions of polymers from which the number-average and weight-average molecular weights were obtained. In this technique a solution of polyethylene polymer sample is injected into a chromatographic column (series) packed with a solid, porous substrate with separates the molecules according to their size in solution. The size-separated molecules are detected and recorded according to their concentration.

A Waters Associates model: 150c ALC/GPC interfaced to an NEC Power Mate SX/16 microcomputer was used. The ASTM Standard: D3593 was the reference method.