

CHAPTER IV

EXPERIMENT

In the present study of the ethylene polymerization on metallocene-methylaluminoxane catalyst, the experiments were divided into four parts:

1. Catalyst and Cocatalyst preparation
2. Ethylene polymerization on the prepared catalyst
3. Characterization of polyethylene products
4. Characterization of hydrated-salt for cocatalyst preparation

The details of the experiments are explained in the following sections.

4.1 CHEMICALS

The chemicals used in this experiment were normal analytical grade, but only critical specifications had to be specified as follows:

1. Ethylene gas (98.5%vol.) was supplied from Union Carbide (Thailand) Limited. It was purified by passing through a column packed with molecular sieve with pore size of 5 Å and diameter of 1 1/6 mm. supplied from Union Carbide (Thailand) Limited to remove traces of moisture before use.

2. Ultra high purity oxygen free nitrogen gas (99.999%vol.) with oxygen and moisture contents both less than 3 ppm was supplied by Thai Industrial Gas Co. Ltd. The gas was purified by passing through the column packed with molecular sieve with poresize of 5 Å to remove moisture before use.

3. Aluminum sulfate octahexahydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ was manufactured by J.T. Baker, USA. Aluminum sulfate hexadecahydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}]$, Aluminum trichloride hexahydrate $[\text{AlCl}_3 \cdot 6\text{H}_2\text{O}]$ was supplied by Fluka Chemika AG., Switzerland. Copper(II) sulphate pentahydrate $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$ was supplied by E. Merck, Federal Republic of

Germany. Natriumthiosulfate pentahydrate $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}]$ was supplied by Riedel-De Haen AG.

4. Bis(cyclopentadienyl)zirconium dichloride $[\text{Cp}_2\text{ZrCl}_2]$ was supplied by Fluka Chemie AG., Switzerland, and used without further purification.

5. Toluene $[\text{C}_7\text{H}_8]$ used as polymerization solvent was supplied from E. Merck, Federal Republic of Germany. Toluene, which was used as the solvent for the polymerization reactions and used in catalyst preparation, was purified by refluxing over sodium (Na) for 12 hours followed by distillation before use. It was kept over sodium metal flakes in glass bottle.

6. Trimethylaluminum $[\text{Al}(\text{CH}_3)_3]$, 2.0 M in toluene was supplied from Nippon Aluminum Alkyls, Ltd., Japan, and used without further purification.

7. Methanol $[\text{CH}_3\text{OH}]$ manufactured by J.T. Baker, USA, was used as catalyst quenching.

4.2 EQUIPMENT

All equipment, used in the catalyst preparation and polymerization, were consisted of five parts as follows:

4.2.1 *Glass Reactor*

The polymerization reactor was a modified glass bottle with a cap having a septum for injection. Its total volume is 250 cm^3 . The reactor was operable in pressure range of 10 to 80 psi. and the temperature range of 27 to 90°C .

4.2.2 *Magnetic Stirrer and Hot Plate*

The magnetic stirrer and hot plate model RCT 13 from KIKA Labortechnik (Germany) were used. They had solid ceramic top which was impact-resistant, acid and alkali resistant. The hot plate can heat to a maximum temperature 200°C , and the stirrer can control the stirring speed from 100 to 1000 rpm.

4.2.3 Cooling System

The cooling equipment was divided into 2 parts, one for cooling the reaction and another for cooling the system. Due to the rapid rate of polymerization at the beginning of the exothermic reaction, the reaction temperature immediately increased and was very high, even the automatic temperature controller could not keep the reaction at the desired temperature. The immersion cooling coil was added. The other cooling system, the Eyela cooling bath model CA 101 from Tokyo Rikakikai (Japan), was used to remove the frictional heat from the mechanical stirring system.

4.2.4 Gas Distribution System

Figure 4.1 is the flow diagram of the polymerization system. The system consisted of: a oxygen-free nitrogen feeding line and an ethylene feeding line. To investigate ethylene consumption rate, a storage ethylene tank was used and connected to the feeding line of the ethylene cylinder. The storage tank was equipped with a pressure gauge to measure the amount of ethylene consumed during the polymerization. A pressure gauge (0-350 psi.) was used for indicating the reaction pressure and two on-off valves were used for gas feeding and releasing.

4.2.5 Syringe, Needle and Septum

The syringe used had a volume of 20, 10, 2, 1 cc. and needle were No. 22, 25, respectively. The septum was a silicone rod. It was used to prevent the surrounding air from entering into glass bottle by blocking at the needle end when transferring a solvent, catalyst and cocatalyst to another glass bottle.

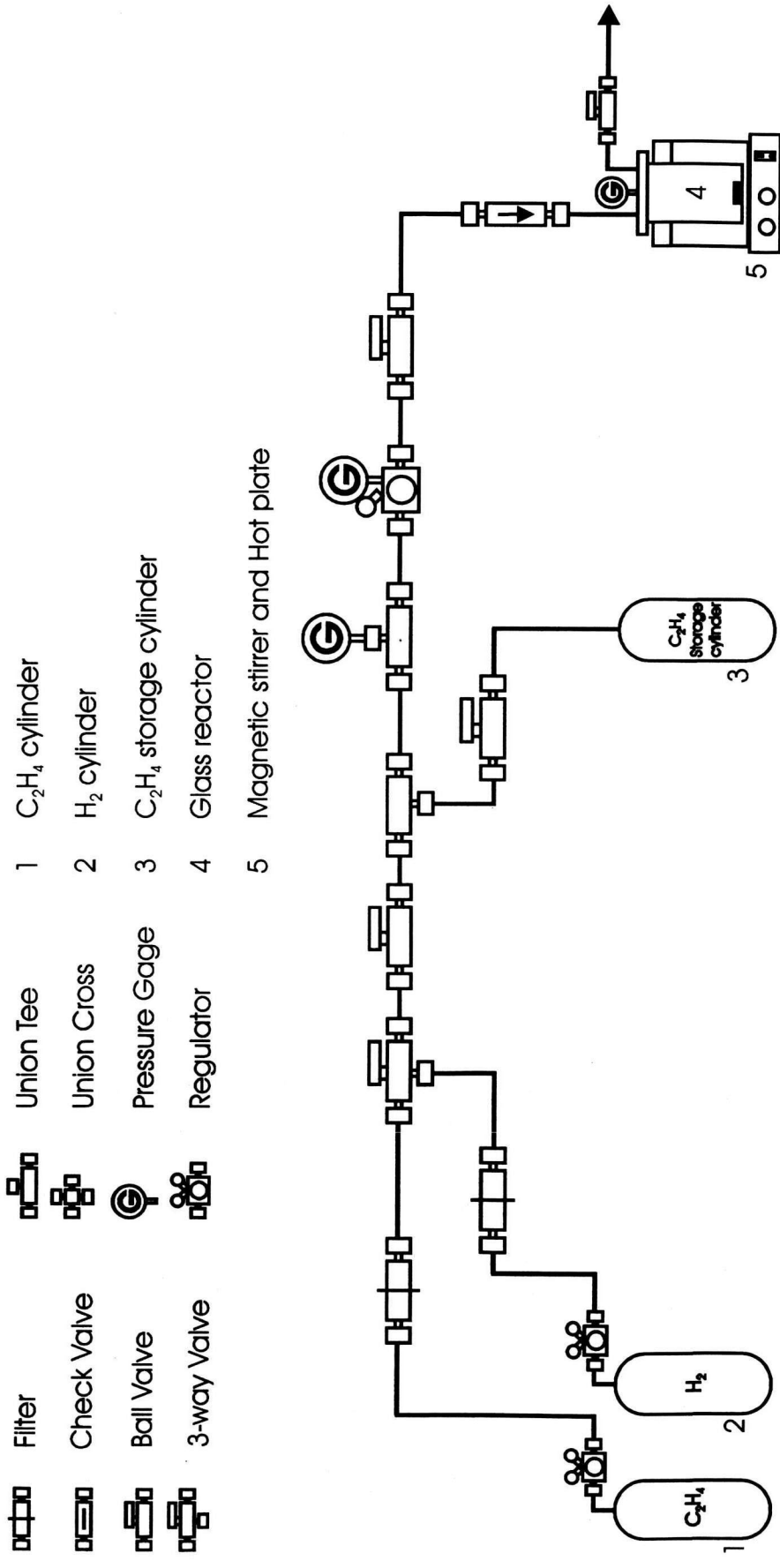


Figure 4.1 Flow diagram of the Polymerization System

4.3 CHARACTERIZATION INSTRUMENTS

The instruments used to characterize the catalysts and polyethylene products were specified in the following:

(a) *Fourier Transformed Infrared Spectroscopy (FT-IR)*

NICOLET FT-IT Impact 400 spectroscopy at Petrochemical Engineering Research Laboratory, Chulalongkorn University, was employed to study the microstructure of polyethylene samples.

(b) *Scanning Electron Microscopy (SEM)*

Scanning Electron Microscope model JEOL at Technological Research Equipment Centre (TREC), Chulalongkorn University was employed to investigate the polyethylene products morphology. The polyethylene products were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

(c) *Differential Scanning Calorimetry (DSC)*

Differential Scanning Calorimeter model 2910 TA Instrument at the Polymer Engineering Research Laboratory, Chulalongkorn University, was applied to determine the melting temperature (T_m) of the polyethylene samples.

(d) *Thermal Gravimetry Analysis (TGA)*

Shimadzu thermal analyzer TGA model 51 at Petrochemical Engineering Research Laboratory, Chulalongkorn University, was applied to measure the capability to give water of hydrated-salt.

4.4 CATALYST AND COCATALYST PREPARATION PROCEDURE

4.4.1 Methylaluminumoxane Cocatalyst Preparation

The methylaluminumoxane can be produced over a wide range of temperatures from above the melting point of the solvent up to the boiling point at the pressure used. Generally, temperatures below about 50 °C are used. Relatively low temperatures can be utilized with the appropriate solvent, say, 0 °C or lower. Pressures are not critical and will typically vary from atmospheric pressure to about 500 psi.

In a 100 ml. glass bottle equipped with a magnetic stirrer and magnetic bar were placed 4.4428 g of aluminum sulfate octahexahydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$. The system was cooled to 0 °C. Next, 60 ml of 2.0 M trimethylaluminum $[(\text{CH}_3)_3\text{Al}]$ (H_2O in crystal : Al = 1:1 by mole) diluted with toluene was added dropwise while keeping the system at 0 °C. After the addition, the slurry was stirred at 5 °C for 20 hr. and at 30 °C for 20 hr. Subsequently, the toluene solution containing methylaluminumoxane was separated from hydrated-salt and used as a stable cocatalyst solution for the polymerization of ethylene with metallocene catalyst.

4.4.2 Metallocene Catalyst Preparation

10 mg of Bis(cyclopentadienyl)zirconium dichloride were dissolved in 50 ml. of toluene under nitrogen atmosphere. The catalyst was shaken until the solution became clear and was used as a catalyst for the polymerization of ethylene with methylaluminumoxane cocatalyst.

4.5 ETHYLENE POLYMERIZATION PROCEDURE

Ethylene polymerization was carried out in a 250 ml. glass reactor, which was equipped with all parts described above and several valves for gas feeding and gas releasing as shown in Figure 4.1. Modified bottle and magnetic bar were dried in oven at 110 °C for 5 hours before used in the ethylene polymerization. In each experiment, 200 ml. of toluene was added to the glass reactor followed by purging with nitrogen at 0.25 bar for 15 min. Then, methylaluminumoxane cocatalyst which was prepared by the method described in section 4.4.1 was injected into the reactor by syringe. Next, the zirconocene catalyst which was prepared by

method described in section 4.4.2 was added into the reactor. The catalyst was then activated by cocatalyst at room temperature for 1 min. in the glass reactor. After that the ethylene gas was passed into the reactor and control pressure was controlled by regulator at constant pressure. The rate of polymerization was determined from ethylene consumption rate measured by the decrease of pressure in ethylene storage cylinder.

After polymerization for 90 min., admission of ethylene gas was stopped and the reactor was depressurized. The reaction was cooled and the polymerization reaction was quenched by adding 25 ml. of methanol. Then the polyethylene was immediately separated by filtration and dried at 110 °C for 24 hours.

The study of ethylene polymerization on metallocene–methylaluminoxane catalyst was divided into two parts. First, the suitable polymerization conditions and their effects on ethylene polymerization were studied on the bis(cyclopentadienyl)zirconium dichloride / methylaluminoxane system. Second, after the optimum condition had been determined, the study of effects of hydrated–salt for the methylaluminoxane preparation was done. The experimental investigation of conditions and effects on the polymerization were conducted as follows:

4.5.1 The Effect of Cocatalyst / Catalyst (Al/Zr) Ratio

The catalyst ratios were varied from 500 to 8000 by mole. The reaction temperature was 300 K and reaction time 90 min. The ethylene partial pressure was 40 psi. The zirconium metal in catalyst suspension was fixed at 8.000×10^{-7} moleZr/litre. The methylaluminoxane was prepared from aluminum sulfate octahexahydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ that supply the water for react with trimethylaluminum to methylaluminoxane and time for preparing a methylaluminoxane was 40 hours.

4.5.2 The Effect of Ethylene Partial Pressure

The polymerization was carried out to investigate the effect of ethylene partial pressure on the catalytic activity. The partial pressure of ethylene was varied from 10 to 70 psi whereas other conditions (i.e. catalyst concentration, reaction time, hydrated–salts for cocatalyst preparation) was kept constant as the best selected from section 4.5.1.

4.5.3 The Effect of Polymerization Temperature

The ethylene polymerization was further studied by varying polymerization temperature at the suitable condition selected from section 4.5.2. The polymerization temperature was varied from 300 to 363 K.

4.5.4 The Effect of Catalyst Concentration

The ethylene polymerization was further studied by varying catalyst concentration at the suitable condition obtained from 4.5.2. The catalyst concentration was varied from 2.3468×10^{-7} to 1.2001×10^{-6} moleZr/litre.

4.5.5 The Effect of Hydrated-Salt for Cocatalyst Preparation

The ethylene polymerization was usually carried out in bis(cyclopentadienyl) zirconium dichloride catalyst with methylaluminoxane cocatalyst system. The aluminum sulfate octahydrate for preparing methylaluminoxane cocatalyst was replaced with other hydrated-salt. In this experiment, aluminum sulfate hexadecahydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}]$, copper(II) sulphate pentahydrate $[\text{CuSO}_4 \cdot 5\text{H}_2\text{O}]$, aluminum trichloride hexahydrate $[\text{AlCl}_3 \cdot 6\text{H}_2\text{O}]$ and natriumtiosulfate pentahydrate $[\text{Na}_2\text{S}_2\text{O}_3 \cdot 5\text{H}_2\text{O}]$ was used to prepare a methylaluminoxane cocatalyst.

4.5.6 The Effect of Time for Preparing Cocatalyst

The ethylene polymerization was further investigated by varying time for preparing the methylaluminoxane cocatalyst under the suitable condition for ethylene polymerization selected from 4.5.2. The time for preparing a cocatalyst was varied from 20 to 80 hours.

4.6 CHARACTERIZATION OF THE POLYETHYLENE PRODUCTS

The polyethylene product has remarkable chemical inertness, particularly at ordinary temperatures to most chemicals, including acids and alkalis [125]. Chemical analysis used to characterize polyethylene was few. As a consequence, a quantitative measurement of physical properties and determination involving chemical and physical structure of polyethylene

have become very important. In this work the polyethylene products were characterized as the following:

4.6.1 Melting Temperature (T_m)

The measurement of the melting temperature of polyethylene samples was performed on a Differential Scanning Calorimeter (DSC). The DSC heater and the sample cells are shown schematically in Figure 4.2. Each composition of the reference and the polyethylene samples was weighed to as close to 15 ± 2 mg as possible. It was then placed in the DSC aluminium pan. The sample was heated from 30°C to 180°C at a constant heating rate of $10^\circ\text{C}/\text{min}$. A DSC scan of the specific energy against the temperature was obtained. The critical point of DSC curve showed the melting temperature of the polyethylene products.

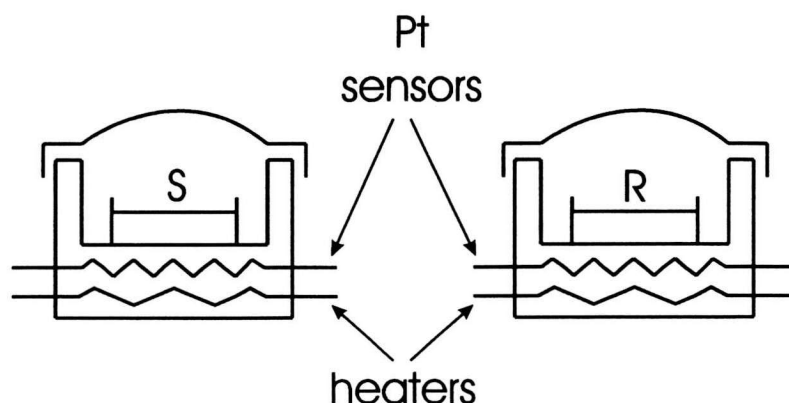


Figure 4.2 The DSC sample cell consists of a sample pan (S) and a reference pan (R)

4.6.2 Microstructure Determination

Infrared spectroscopic techniques are suited for the determination of microstructure of polymer such as methyl groups. In practice, conversion of infrared adsorption intensities to concentration values are made by use of absorptivities calculated from model compound. Figure 4.3 shows the polyethylene spectrum [126]. There are three very strong bands at 2920 , 1460 and $720/730\text{ cm}^{-1}$. These are assignable to the C-H stretching, deformation and rocking modes of $-(\text{CH}_2)_n-$ groups respectively. The band at 1378 cm^{-1} is the amount of chain branching in the polyethylene.

In addition to chain branching there is a second type of defect structure, occasional double bonds. These are readily identified by out-of-plane deformation mode. Polymer from the Phillips process have one end of each chain terminating by vinyl group,

which gives the sharp band at 910 cm^{-1} [125]. Low density polyethylene (LDPE) from high pressure process contained vinylidene groups, which absorbs at 890 cm^{-1} [125], while polyethylene prepared from metallocene-alkylaluminum catalyst has frequently a combination of three types of unsaturation, the two ones already mentioned together with trans $\text{CH}=\text{CH}-$, characterized by a band at 965 cm^{-1} [125].

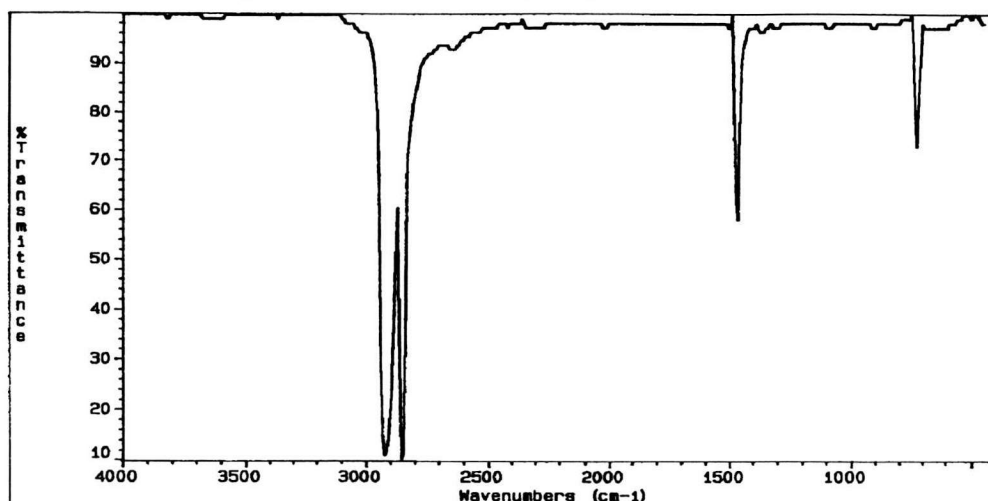


Figure 4.3 Infrared spectrum of high density polyethylene [126].

4.6.3 Morphology

The term of morphology was referred to the shape, texture, or form of polyethylene. The polymer samples were coated with gold by ion sputtering device. Scanning Electron Microscopic (SEM) technique was the effective method to investigate these morphologies.

4.6.4 Rate of Ethylene Polymerization (r_p)

The ethylene consumption during the polymerization time was expressed as a curve of gram of ethylene consumed at room temperature per gram of catalyst versus time ($\text{gPe/gZr}\cdot\text{atm}\cdot\text{hr}$). The ethylene consumption can be calculated from decreasing of ethylene pressure in C_2H_4 storage cylinder.

4.7 CHARACTERIZATION OF HYDRATED-SALTS FOR COCATALYST PREPARATION

The water content of the hydrated-salt was analyzed by Shimadzu Thermal analyzer TGA model 51. Hydrated-salts (about 18 mg) was placed in a TGA platinum pan and heated from room temperature to 550 °C with a constant heating rate of 10 °C/min with N₂ gas flowing at 50 ml/min. The temperature was kept at 550 °C for 25 min until hydrated-salts weight constant because water in lattice was desorbed. A TGA plot of the weight against the temperature was obtained. It also showed the water releasing rate of hydrated-salt samples.