CHAPTER IV
EXPERIMENT

In the present study of the influence of supported zirconocene catalyst on ethylene polymerization, the experiments were divided into four parts:

(i) Catalyst preparation

(ii) Ethylene polymerization on the prepared catalyst

(iii) Characterization of catalyst precursor

(iv) Characterization of polyethylene products

The details of the experiments were explained below.

4.1 Chemicals

The chemicals used in this experiment were analytical grade, but only critical materials were specified as follows:

1. Ethylene gas (99.96%) was donated from National Petrochemical Co., Ltd., Thailand and purified by passing through columns containing NaOH, P_2O_5, and molecular sieve 4A, respectively.

2. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd. and further purified by passing through columns packed with copper catalyst, NaOH, P_2O_5, and molecular sieve 4A to remove traces of oxygen and moisture.

3. Toluene was donated from EXSOL Chemical Ltd., Thailand. This solvent was dried over dehydrated $CaCl_2$ and distilled over sodium/benzophenone under argon atmosphere before use.

4. Trimethylaluminum [$Al(CH_3)_3$] 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan, and used without further purification.

5. Methylaluminoxane (MAO) 1.5092 M in toluene was donated from Tosoh Akzo, Japan. Dried MAO was prepared by drying MAO in vacuum at room temperature.

6. Silicon tetrachloride ($SiCl_4$) was supplied from Fluka Chemie A.G., Switzerland and used as received.

7. Trichloromethylsilane (Cl_3SiCH_3) obtained from Tokyo Kasei, Japan was used as received.

8. Dimethyldichlorosilane [$Cl_2Si(CH_3)_2$] was purchased from Fluka Chemie A.G., Switzerland and used without further treatment.

9. Trimethylchlorosilane [$ClSi(CH_3)_3$] was supplied from Fluka Chemie A.G., Switzerland and used as received.

10. Sodiumhydrogencarbonate purchased from Fluka Chemie A.G., Switzerland was used as received.

11. Silica gel from Fuji Silasia Chemical Ltd. (Cariact P-10, surface area 300m^2/g) was calcined at 400°C for 6 hours.

12. Bis(cyclopentadienyl)zirconium dichloride (Cp_2ZrCl_2) was manufactured from Fluka Chemie A.G., Switzerland and used without further purification.

4.2 Equipments

All equipments, used in the catalyst preparation and polymerization, were listed as follows:

4.2.1 Schlenk Line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and pump, respectively. The argon line was connected to the trap and the mercury bubbler that was a manometer tube and contain enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in Figure 4.1.

4.2.2 Schlenk Tube

A tube with a ground glass joint and a side arm which was three way glass valve as shown in Figure 4.2. Size of the Schlenk tubes were 50, 100, and 200 ml used to prepare catalyst and collect materials which were sensitive to oxygen and moisture.

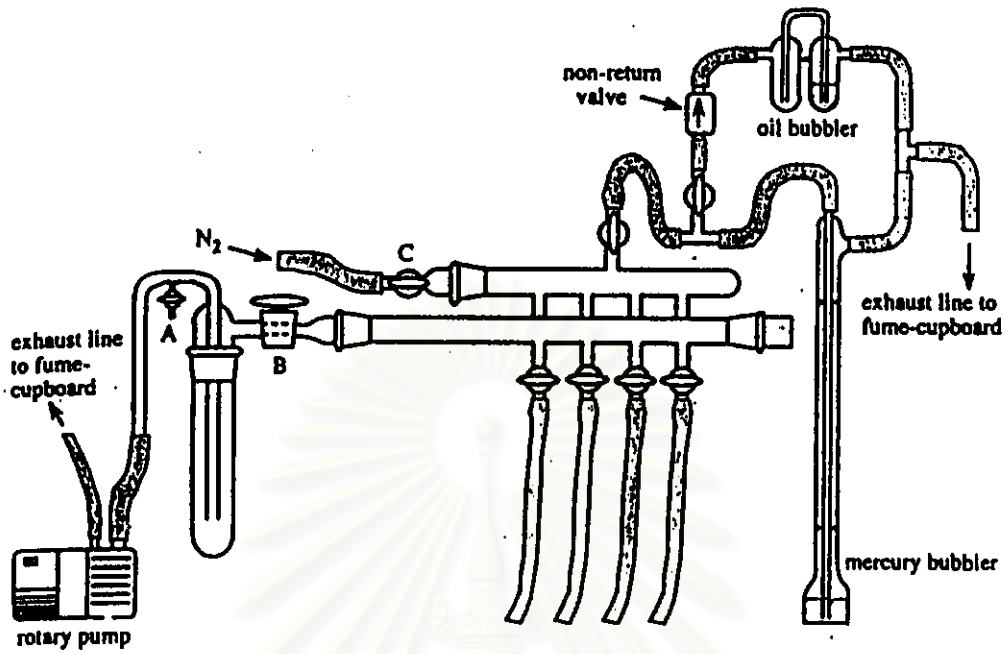

Figure 4.1 Schlenk line

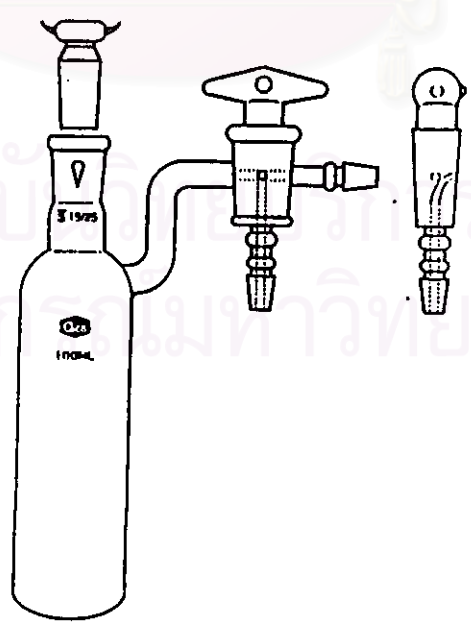

Figure 4.2 Schlenk tube

4.2.3 Reactor

A 100 ml stainless steel autoclave was used as the polymerization reactor.

4.2.4 Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from IKA Labortechnik were used.

4.2.5 Cooling System

The cooling system was used in the solvent distillation for condensing the freshly evaporated solvent.

4.2.6 Vacuum Pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

4.2.7 Inert Gas Supply

The inert gas (argon) was passed through columns of supported copper metal catalyst as oxygen scavenger, NaOH, P_2O_5, and molecular sieve 4A to remove moisture. The oxygen scavenger was regenerated by treatment with hydrogen at 300 °C for 2 hours before flowing the argon gas through all of the above columns.

4.3 Characterizing Instruments

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

4.3.1 Fourier Transformed Infrared Spectroscopy (FT-IR)

Nicolet FT-IR Impact 400 Spectrophotometer at the Petrochemical Engineering Research Laboratory, Chulalongkorn University was employed to study the chemical structure of polyethylene products.

4.3.2 Scanning Electron Microscope (SEM)

SEM observation with a JSM-640 Scanning Microscope, Microspec WDX at Technological Research Equipment Centre, Chulalongkorn University was employed to investigate the morphology of catalyst precursor and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen.

4.3.3 Differential Scanning Calorimetry (DSC)

The melting temperature (Tm) and crystallinity of polyethylene were determined by a Perkin-Elmer DSC 7 at Bangkok Polyethylene Public Company Limited. The analyses were performed at heating rate of 10°C/min. in the temperature range 30-200°C. The heating cycle was run twice. The first scan, samples were heated and then cooled to room temperature. The second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of samples.

4.3.4 Gel Permeation Chromatography (GPC)

Molecular weights and molecular weight distributions of the produced polyethylene were measured at 135°C using 1,2,4-trichrolobenzene as solvent by a Water 150-C Gel Permeation Chromatograph at Bangkok Polyethylene Public Company Limited. The GPC instrument was equipped with a viscometrical detector; differential optical refractometer, and three Styragel HT type columns (HT3, HT4,

and HT5) with a $1x10^7$ exclusion limit for polystyrene. The columns were calibrated with standard narrow molar mass distribution polystyrenes and linear low density polyethylenes and polystyrenes.

4.4 Catalyst Preparation Procedure

All reactions were carried out under argon atmosphere using Schlenk techniques and glove bag.

4.4.1 Preparation of the Modified Silica Gel

To a suspension of 940 mg of calcined SiO_2 in 10 ml of toluene was added 10 ml of a toluene solution containing 1 mmol of $Cl_2Si(CH_3)_2$ under argon atmosphere. The reaction mixture was refluxed for 7 hours under stirring with a magnetic stirrer. The resulting silica gel was filtered and washed five times with 20 ml of toluene, and then to the silica gel in 20 ml of toluene was added $1.8x10^{-2}$ ml of 1.5 N aqueous sodium hydrogencarbonate solution under argon atmosphere. The mixture was kept standing at room temperature for 7 hours with rigorous stirring. The solid part was separated by filtration, washed five times with 20 ml of toluene and dried in vacuo at room temperature to obtain the modified silica gel.

4.4.2 Preparation of the Catalyst Precursor

The modified silica gel prepared above was reacted with 16 mmol of MAO in 10 ml of toluene at room temperature for 30 minutes. The solid part was separated by filtration and washed five times with 20 ml of toluene, followed by drying in vacuo at room temperature to obtain the catalyst precursor.

4.4.3 Ethylene Polymerization Procedure

The ethylene polymerization reactions were carried out in a 100 ml stainless steel autoclave equipped with a magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110°C for 30 minutes and purged with argon 5 times in glove bag before used in the polymerization of ethylene. Toluene, 100 mg of the catalyst precursor, and mixture of a prescribed amount of Cp_2ZrCl_2 and TMA

stirred for 5 minutes at room temperature were introduced into the autoclave, respectively under argon atmosphere. The Total volume of mixture solution was 15 ml The whole mixture was allowed to aging for 10 minutes at room temperature. The reactor was frozen in liquid nitrogen to stop reaction, and then the autoclave was degassed. The polymerization was started by feeding ethylene gas. The reaction of polymerization was terminated by addition of acidic methanol. The precipitated polymer was washed with methanol and dried in the oven at 110°C for 6 hours. Each polymerization was repeated to ensure reproducibility.

The various effects on the ethylene polymerization with silica-supported metallocene catalyst and optimized conditions were investigated. The effects of polymerization on production of polyethylene were systematically varied as follows.

4.4.3.1 The Effect of Cocatalyst/Catalyst (Al/Zr) Molar Ratio

The Al/Zr molar ratios were varied from 500 to 5000. The concentration of Cp_2ZrCl_2 was fixed at 6.6667×10^{-5} M (1ml of 1×10^{-3} M Cp_2ZrCl_2 in a toluene solution) and ethylene pressure was introduced at 80 psi. The polymerization reaction was kept constant at 40°C for 30 minutes.

4.4.3.2 The Effect of Catalyst Concentration

The concentrations of Cp_2ZrCl_2 catalyst were investigated between 1×10^{-4} and 3.333×10^{-5} M. Pressure of monomer, temperature and time of polymerization were operated constantly at 80 psi, 40°C, and 30 minutes, respectively whereas the Al/Zr molar ratio was kept constant following the best result in Section 4.4.3.1.

4.4.3.3 The Effect of Polymerization Temperature

The ethylene polymerization was further studied by varying the polymerization temperature from 30 to 90°C using the suitable condition selected from Section 4.4.3.2.

4.4.3.4 The Effect of Ethylene Pressure

The Al/Zr molar ratio, Cp_2ZrCl_2 concentration, and polymerization temperature were carried out as the best result of Sections 4.4.3.1 to 4.4.3.3 The ethylene pressures were tested between 10 to 80 psi.

4.4.3.5 The effect of various silane compounds used for the modified silica preparation

The ethylene polymerizations were carried out using the catalyst precursor treated with various silane compounds viz, $ClSi(CH_3)_3$, Cl_3SiCH_3, and $SiCl_4$ to prepare the modified silica. The conditions of polymerization were kept constant following the best result of Sections 4.4.3.1 to 4.4.3.4.

4.5 Characterization of Catalyst Precursor

4.5.1 Morphology

Scanning Electron Microscopic (SEM) technique was the effective method to investigate these morphologies. The term of morphology was referred to the shape, texture, or form of catalyst precursor.

4.6 Characterization of Polyethylene Products

The polyethylene product has remarkable inertness to most chemicals including acid and alkaline, particularly at ordinary temperature. For this reason, there were few of chemical analysis procedure available for characterization of polyethylene. Therefore, the quantitative measurements of physical properties and determinations of the involved chemicals and physical structure have become increasingly important. In this work, the obtained polyethylenes were characterized by the following methods.

4.6.1 Chemical Structure Determination

4.6.1.1 Infrared Spectroscopy (IR)

The infrared spectroscopic technique was widely used to characterize polymer structure. Comparison of the positions of absorption in the IR spectrum of a polymer sample with the characteristic absorption led to identification of the bands and functional groups presented in the polymer. The IR spectrum of a polymer was unique which can be considered as a 'fingerprint'.

4.6.2 Morphology

The morphology of the polyethylene obtained was observed with Scanning Electron Microscopy (SEM).

4.6.3 Melting Temperature (Tm)

Differential Scanning Calorimetry (DSC) was an instrument designed to measure the thermal properties especially melting temperature (Tm). The melting temperature of polyethylenes were determined the critical point of DSC curve.

4.6.4 Crystallinity (%χ)

Crystallinity of produced polymer can be evaluated using differential scanning calorimetry technique by calculating from heat of fusion of the sample (ΔH_m).

4.6.5 Average Molecular Weight and Molecular Weight Distribution

One of the most widely used methods for the routine determination of molecular weight (Mw) and molecular weight distribution (MWD) was gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography (SEC) to separate samples of polydisperse polymers into fractions of narrower molecular weight distribution. Basic instrumentation for GPC analysis was shown in Figure 4.3.

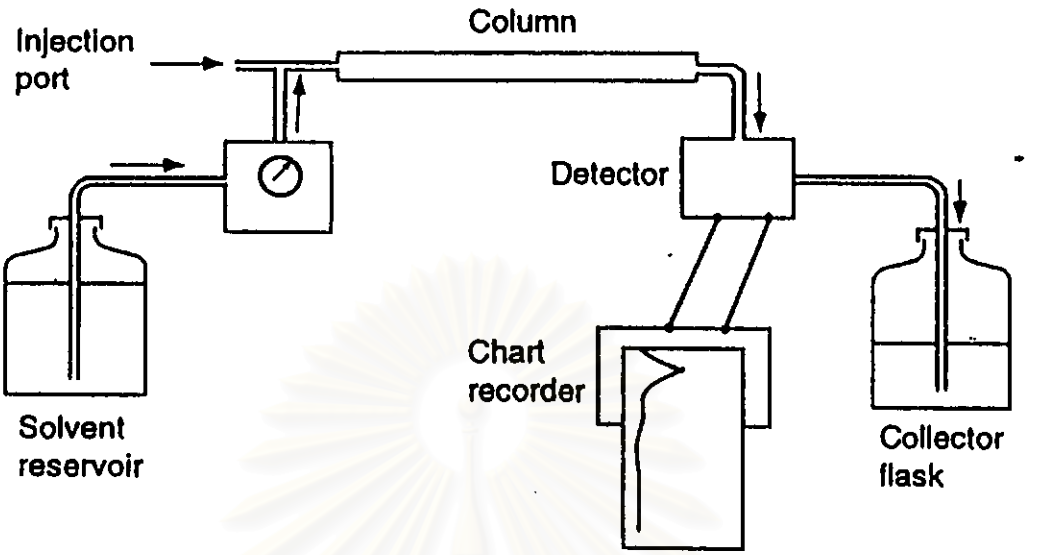

Figure 4.3 Basic Instrumentation for Gel Permeation Chromatography (GPC)

4.6.6 The Comparison of Commercial Ziegler-Natta Catalyst and SiO_2/ Silane/MAO-Cp_2ZrCl_2/TMA Catalyst System

The catalytic activity of SiO_2/ Silane/MAO-Cp_2ZrCl_2/TMA Catalyst System was compared to that of the commercial Ziegler-Natta catalyst. Besides the activity, polymers produced with both of these systems were also considered.