CHAPTER III
EXPERIMENT

3.1 Chemicals

The chemicals used in these experiments were analytical grade, but only critical materials were specified as followed:

1. Propylene gas (C_3H_6) was donated from National Petrochemical Public Company Limited (NPC), used without further purification.

2. Argon gas (Ultra High Purity, 99.999%) was purchased from Thai Industrial Gas Co., Ltd. (TIG) and was purified by passing through the column packed with molecular sieve 3 Å, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) to remove traces of oxygen and moisture.

3. Hexane (C_6H_{14}) polymerization grade was received from Esso chemical (Thailand) Co., Ltd. It was dried over dehydrated $CaCl_2$ and was distilled over sodium/benzophenone under argon atmosphere.

4. Heptane (C_7H_{14}, 99.84%) was purchased from J.T., Baker and used as solvent for polymer extraction without further purified.

5. Titanium tetrachloride ($TiCl_4$, > 99%) was purchased from MERK.

6. Triethylaluminum ($Al(C_2H_5)_3$) ,diluted in hexane, was donated from Bangkok Polyethylene Co.,Ltd. (Thailand).

7. Anhydrous magnesium chloride ($MgCl_2$, >98%) was purchased from Sigma.

8. Diethylphthalate ($C_{12}H_{14}O_4$, 98%) was supplied from Fluka Chemical Industries.

9. 2-Ethylhexanol ($C_8H_{18}O$, >99%) was received from Fluka Chemical Industries.

10. Pthalicanhydride ($C_8H_4O_3$, >97) was received from Fluka Chemical Industries.

11. Decane ($C_{10}H_{22}$,>98%) was supplied from Fluka Chemical Industries.

12. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.

13. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.

14. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.

15. Methanol (Commercial grade) was purchased from SR lab.

16. Methylaluminoxane (MAO) 2.598 M in toluene was donated from Tosoh Akzo, Japan.

17. racemic-Ethylenebis(indenyl)zirconium dichloride (rac-Et[Ind]$_2$ZrCl$_2$) was obtained from Aldrich chemical Company, Inc.

18. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.

19. Toluene was donate from Exxon Chemical Co., Ltd., Thailand.

20. Xylene (99.8%) was purchased from Merck.

21. Trimethylaluminum (TMA) 2 M in toluene was donated from Nippon Aluminum Alkyls Co., Ltd., Japan.

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

3.2 Equipments

All types of equipments used in the catalyst precursor preparation and polymerization are listed below:

3.2.1 Cooling System

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

3.2.2 Glove box

Including oxygen and moisture analyzer for transferring solid reagents under inert atmosphere and for storing air-sensitive reagents. The oxygen and moisture levels are normally below 2 ppm inside the glove box.

3.2.3 Inert Gas Supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3A to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 ^{o}C overnight before flowing the argon gas through all the above columns. The inert gas supply system is shown in Figure 3.1.
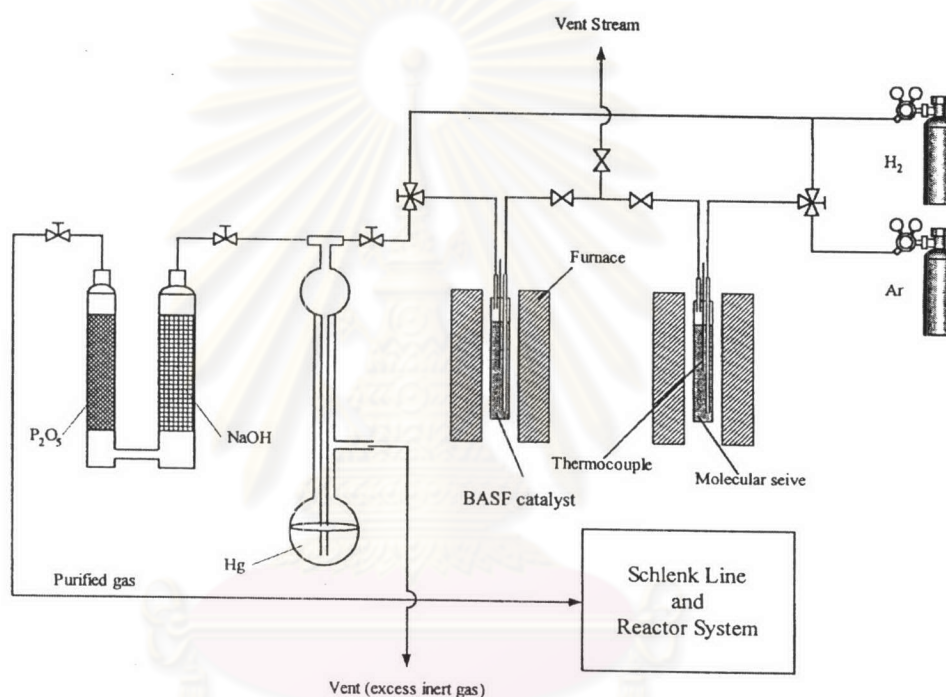

Figure 3.1 Inert gas supply system

3.2.4 Magnetic Stirrer and Heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

3.2.5 Reactor

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

3.2.6 Schlenk Line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with 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 3.2.
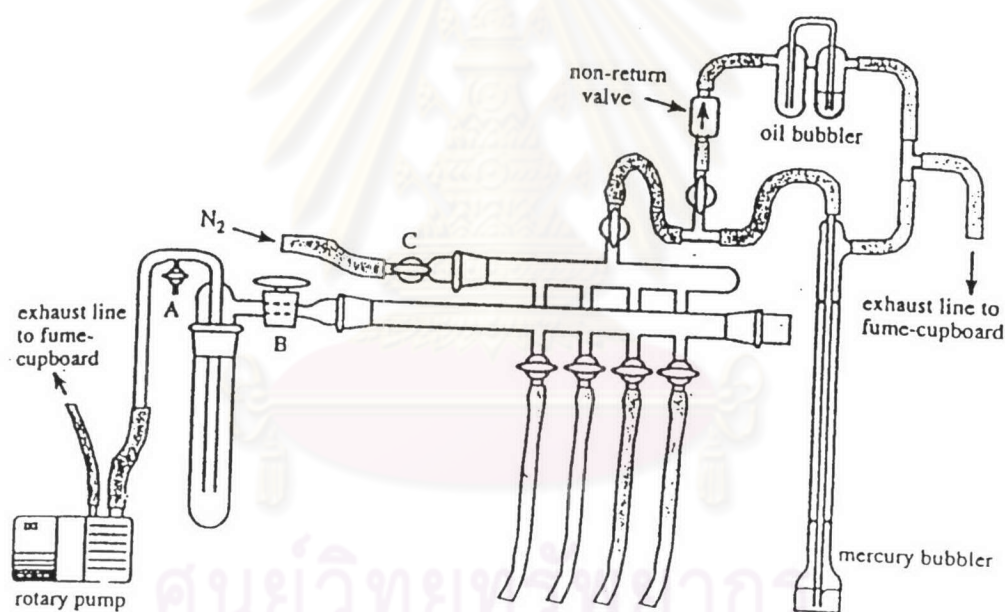

Figure 3.2 Schlenk line

3.2.7 Schlenk Tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 3.3. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture
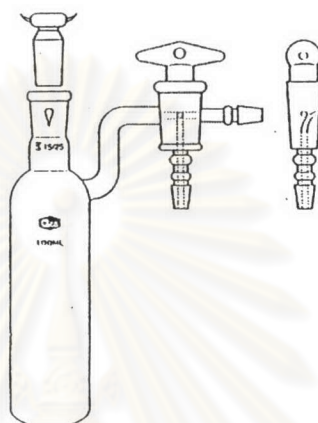

Figure 3.3 Schlenk tube

3.2.8 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.

3.3 Preparation of Catalyst Precursors

3.3.1 Preparation of Ziegler-Natta Precursor

0.476 g of Anhydrous magnesium chloride, 2.5 ml of decane and 2.34 ml of 2-ethylhexanol were reacted at 130 °C for 2 hours to form a uniform solution. Phthalic anhydride 0.109 g was added to solution, and the mixture was stirred at 130 °C for 1 hour to dissolve phthalic anhydride. The resulting, uniform solution was cooled to room temperature, and wholly drop wise over the course of 1 hour to 20 ml of titanium tetrachloride kept at -20 °C. After the addition, the mixture was heated to 110

°C over the course of 4 hours. When the temperature reached 110 °C, 0.26 ml of diethylpthalate was added. The mixture was maintained at this temperature for 2 hours. After the reaction for 2 hours, the solid portion was collected from the reaction mixture. The solid portion was again suspended in 20 ml of titanium tetrachloride and again reacted at 120 °C for 2 hours. After the reaction, the solid portion was again collected then washed with 10 ml of decane and with 10 ml of hexane 3 times. The resulting solid was dried in vacuum.

3.3.2 Preparation of Metallocene Catalyst Precursor

Silica gel was calcined under vacuum at 400 °C for 6 hours. Calcined silica 1 g was reacted with the desired amount of MAO in 10 ml of toluene at room temperature for 30 minutes. The solid part was separated and washed 5 times with 20 ml of toluene, followed by drying in vacuum at room temperature to obtain the catalyst support precursor SiO_2/MAO.

3.4 Propylene Polymerization Procedure

The propylene polymerization reactions were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110 °C for 30 minutes before use. Solvent, catalyst precursor, catalyst and cocatalyst were introduced into the autoclave and stirred for 5 minutes at room temperature in the glove box. After that, the reactor was frozen in liquid nitrogen to stop reaction and then the autoclave was evacuated to remove the argon, and the reactor was placed in the water bath to control the temperature. The polymerization was started by feeding propylene gas. The polymerization was carried out for 90 minutes, and then stopped the polymerization by venting propylene gas and adding acidified methanol. The precipitated polymer was washed with methanol and dried at room temperature.

In case of metallocene catalyst, polymerization was performed at 5×10^{-5} M catalyst concentration, 2000 $Al_{(TMA)}$, $Al_{(MAO)}/Zr$ ratio, 60 ºC, 40 psi and used toluene as solvent.

For Ziegler-Natta catalyst, propylene polymerization was carried out at 7×10^{-5} M catalyst concentration, 167 $Al_{(TEA)}/Ti$ ratio, 60 ºC, 40 psi and used hexane as solvent.

The various effects of polymerization conditions on propylene polymerization using two different catalyst systems, metallocene and Ziegler-Natta catalyst, were studied as follows.

3.4.1 The Effect of Solvent

The influence of solvent was studied by varying types of solvent such as hexane, toluene, heptane and xylene. In case of Ziegler-Natta catalyst, liquid fraction obtained at the same conditions as polymerization conditions without monomer was characterized by FT-IR to analyzed the composition in liquid.

3.4.2 The Effect of Polymerization Temperature

The propylene polymerization was studied by varying the polymerization temperature from 40 to 70 ºC using the selected conditions from above.

3.4.3 The Effect of Polymerization Pressure

To investigate the effect of polymerization pressure. The polymerization pressure was varied from 40 psi to 100 psi for both catalysts.

3.4.4 The Effect of Catalyst Concentration

The concentrations of catalyst were investigated at 5×10^{-5} to 8×10^{-5} M. for both metallocene and Ziegler-Natta catalyst. The polymerization conditions were used from above and were kept constant for 90 minutes.

3.5 Polymer Characterization

3.5.1 Differential Scanning Calorimetry (DSC)

The melting temperature and glass transition temperature of the polymer was determined with a Perkin-Elmer DSC 7 at Central Instrument Facility Faculty of Science, Mahidol University. The analyses were performed at heating rate 10°C/min in the temperature range 50-200°C. The heating cycle was run twice. In the first scan, samples were heated up and then cooled down to 50°C. In the second scan, samples were reheated at the same rate. Only the results of the second scan were reported because the first scan was influenced by the mechanical and thermal history of the samples.

3.5.2 Scanning Electron Microscope (SEM)

All distribution on the catalyst support precursor and polymer particles were investigated by Scanning Electron Microscope (SEM), JSM-640 Scanning Microscope, Microspec WDX at Technological Research Equipment Center, Chulalongkorn University, with Energy Dispersive X-ray analysis (EDX).

3.5.3 Soxhlet-Type Extractor

Soxhlet-Type extractor was used to determine the isotactic content of polypropylene. The obtained polymer was weighed in cellulose timber then was extracted in Soxhlet-Type extractor using heptane as solvent for 6 hours. The fraction of insoluble polymer over whole polymer x 100 was defined as percent index of isotacticity (%I.I.).

3.5.4 ^{13}C-Nuclear Magnetic Resonance (^{13}C-NMR)

^{13}C-NMR spectroscopy was used to determine the polymer microstructure. Sample solutions were prepared in 1,2,4-trichlorobenzene and benzene-d_6 for internal

lock signal. The ^{13}C-NMR spectra were obtained at 100°C using Bruker Biospin Avance DPX-400 operating at 100 MHz at the Department of Science Service.

3.5.6 Fourier Transformed Infrared Spectroscopy (FT-IR)

The infrared spectroscopic technique was widely used to characterize polymer structure. Comparison of the position 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'. Nicolet FT-IR Impact 400 Spectrophotometer at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, Department of Chemical Engineering, Chulalongkorn University was employed to study the chemical structure of liquid fraction to study the effect of solvent.