CHAPTER III

EXPERIMENTAL

3.1 Chemicals

3.1.1 Chemical 1

The chemicals used in these experiments, carried out at the Center of Excellence on Catalysis and Catalytic Reaction Engineering, were specified as follows:

1. Polymerization-grade propylene (C_3H_6) was used as received from PTT Chemical Plc. (Thailand)
2. Ultra high purity argon (99.999%) was purchased from Thai Industrial Gas Co., Ltd. (TIG) and was further purified by passing through the column packed with molecular sieve 3Å, BASF Catalyst R3-11G (copper catalyst), sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture.
3. Anhydrous magnesium chloride ($MgCl_2$, >98%) was purchased from Sigma-Aldrich Inc. and was vacuum dried at 120°C for 6 h before use.
4. CaO were purchased from Merck Ltd.
5. Cariact P-10 Silica gel (specific surface area 300 m^2/g), supplied by Fuji Silasia Chemical, was calcined at 400°C under vacuum for 6 h before use.
6. Phthalic anhydride ($C_8H_4O_3$, >97) was received from Fluka Chemie A.G. Switzerland
7. Diethylphthalate ($C_{12}H_{14}O_4$, 98%) was supplied from Fluka Chemie A.G. Switzerland and used as an internal donor.
8. 2-Ethyl-1-hexanol ($C_8H_{18}O$, >99%) was purchased from Fluka Chemie A.G. Switzerland.
9. Titanium tetrachloride ($TiCl_4$, > 99%) was purchased from MERK.
10. Triethylaluminum ($Al(C_2H_5)_3$) in hexane solution, was donated from PTT Chemical Plc., (Thailand)

11. Methylaluminoxane (MAO) in toluene solution was donated by Tosoh Akzo Corp.
12. Modified methylaluminoxane (MMAO) in toluene solution was donated by Tosoh Akzo Corp.
13. Polymerization-grade *n*-hexane (C_6H_{14}) was donated from Exxon chemical Thailand Ltd. It was dried over dehydrated $CaCl_2$ and was purified by refluxing over sodium/benzophenone under argon atmosphere prior to use.
14. *n*-Heptane (C_7H_{14}, 99.84%) was supplied from Fluka Chemie A.G. Switzerland and was used as solvent for polymer extraction.
15. *n*-Decane ($C_{10}H_{22}$, >98%) was supplied from Fluka Chemical Industries.
16. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
17. Sodium (lump in kerosene, 99.0%) was supplied from Aldrich chemical Company, Inc.
18. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.
19. Xylene (99.8%) was purchased from Merck.
20. Commercial-grade methanol was purchased from SR lab.
21. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma-Aldrich Inc.

3.1.2 Chemical 2

The chemicals employed during the experimental research at Terano Laboratory, Japan. Only critical materials are summarized in the following lists:

1. Propylene of research grade, donated by Chisso Corp., was used without further purification.
2. Anhydrous grade of methanol, ethanol, 1-butanol, acetone and ethylacetate, purchased from Wako Pure Chemical Industries Ltd., were used after degassed, dehydrated with molecular sieves 4Å and stored under argon atmosphere.
3. Ethylbenzoate (EB), purchased from Wako Pure Chemical Industries Ltd., was used after dehydration with molecular sieves 13X under a nitrogen atmosphere.

4. Anhydrous magnesiumethoxide ($Mg(OEt)_2$) donated by Toho Titanium Co. Ltd. and used without further purification.
5. Titaniumtetrachloride ($TiCl_4$) purchased from Wako Pure Chemical Industries Ltd. and used as received.
6. Triisobutylaluminium (TIBA) was donated by Tosoh Akzo Corp.
7. High purity nitrogen, purchased from Uno Sanso Co., was used without further purification.
8. *n*-Heptane and toluene, purchased from Wako Pure Chemical Industries Ltd., as solvents were purified by passing through molecular sieves 13X column.

3.2 Apparatus

3.2.1 Gas Purification System

Argon (UHP) was further purified by passing through the column packed with molecular sieve 3Å, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) in order to remove traces of oxygen and moisture prior to use. The BASF catalyst was treated with mixed Ar/H_2 (H_2 3%) at 300°C overnight in order to regenerate the catalyst. The inert gas purification system is given in Figure 3.1.

3.2.2 Glove Box

The VAC Glove box which is a controlled atmosphere apparatus provides an inert environment for handling highly reactive materials. It comprises gas purification system and closed loop gas recirculation to remove O_2 and H_2O. Moreover, oxygen and moisture analyzer is equipped to monitor trace oxygen and moisture content of which acceptable level is less than 5 ppm.

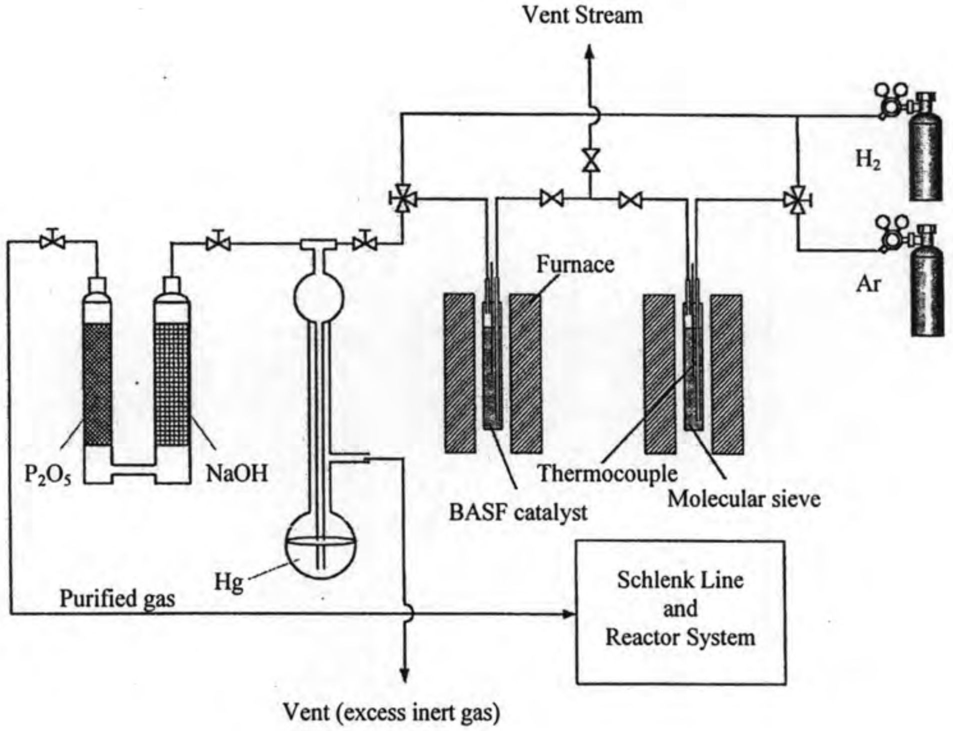

Figure 3.1 The inert gas purification system.

3.2.3 Schlenk Technique

A dual manifold design model of Schlenk line, which is consisted of one manifold for vacuum and another for inert gas, is used as a workhouse item for the manipulation of air-sensitive materials. The argon line is connected with mercury bubbler at which a manometer tube is contained enough mercury to provide a seal from the atmosphere when argon line is evacuated. A tube with a ground glass joint and side arm, which is three-way glass valve as illustrated in Figure 3.2. It permits the user to pull a vacuum on the tube or to fill it with an inert atmosphere. Sizes of Schlenk tubes are 50, 100 and 200 ml used to prepare catalyst and store materials which are sensitive to oxygen and moisture.

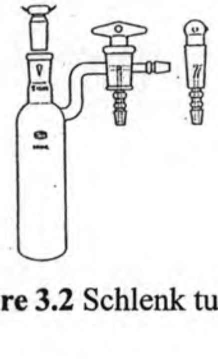

Figure 3.2 Schlenk tube.

3.3 Preparation of Catalyst Precursors

3.3.1 Catalyst 1: $TiCl_4/DEP/MgCl_2$

A catalyst of type $TiCl_4/DEP/MgCl_2$ was synthesized via recrystallization method according to a reported procedure [36]. Under an argon atmosphere and magnetic stirring, a mixture of 0.476 g (5 mmol) of anhydrous $MgCl_2$ and 2.5 ml of *n*-decane were treated with 2.34 ml (15 mmol) of 2-ethyl-1-hexanol at 130°C for 2 h then added 0.1089 g (0.74 mmol) of phthalic anhydride and held at the temperature for one more hour. Consequently, this suspension became to clear solution. After the system was cooled to -20°C, about 20 ml (182.2 mmol) of $TiCl_4$ was injected dropwise over a period of 1 h in order to confirm recrystallization of $MgCl_2$ by removing the added compound before heating slowly at an average rate of 0.5°C/min to 110°C over a period of 4 h followed by treatment of the solution in the presence of 0.26 ml (1.3 mmol) of diethylphthalate (DEP) at 110°C for 2 h. The resulting solid product was separated by filtration and the addition of 20 ml of $TiCl_4$ was repeated at room temperature. After heating and keeping the solution at 120°C for 2 h, the liquid was siphoned off and the solid part was washed twice with 10 ml of *n*-decane and three portions of *n*-hexane 10 ml, respectively. The obtained solid catalyst was vacuum dried at 40°C for 30 min and contained 3% Ti by means of ICP analysis.

3.3.1 Catalyst 2: $TiCl_4/EB/MgCl_2$

A monoester-type catalyst $TiCl_4/EB/MgCl_2$ was prepared by a chemical reaction procedure without mechanical treatment (e.g. ball milling). $TiCl_4$ was reacted with a mixture of $Mg(OEt)_2$ and EB in the following procedure: $Mg(OEt)_2$ (40 g) and $TiCl_4$ (80 ml) in toluene (320 ml) were heated up to 90°C, mixed with EB (12 ml) and reacted at 90°C under stirring for 2 h. The mixture was washed twice with toluene and reacted again with $TiCl_4$ (80 ml) in toluene (320 ml) at 90°C for 2 h. After the reaction, the catalyst was precipitated followed by the decantation. Then, the catalyst obtained was washed with heptane for several times, and then used as heptane slurry. Ti content was 3 wt% determined by the titration method.

3.4 Preparation of SiO_2-Supported Aluminoxanes

3.4.1 Methylaluminoxane (MAO)/SiO_2

Silica gel was heated under vacuum at 400°C for 6 h. Then, 1 g of calcined silica was reacted with 40 ml of MAO in additional 10 ml of toluene for 30 min at room temperature. The solid part was washed five times with 20 ml of toluene and then dried under vacuum to obtain MAO/SiO_2 powder.

3.4.2 Modified Methylaluminoxane (MMAO)/SiO_2

The preparation of MMAO/SiO_2 was pretty much similar to that of the MAO/SiO_2. MMAO was used as a starting material instead of MAO.

3.4.3 dried-Modified Methylaluminoxane (dMMAO)

dMMAO was prepared according to the method as described in the literature [166]. The toluene solution of 40 ml MMAO was vacuum dried at ambient temperature for 6 h followed by dissolving with *n*-heptane and dried under vacuum for removing the residue of Me_3Al (TMA) and *i*-Bu_3Al (TIBA). After repeating this procedure for 5 times, the obtained solid particle was named as dMMAO.

3.4.4 dried-Modified methylaluminoxane (dMMAO)/ SiO_2

For preparation of dMMAO/SiO_2, dMMAO was treated with 1 g of SiO_2 in toluene solution for 30 min and again evacuated. The solid part was washed five times with 20 ml of *n*-heptane and then dried under vacuum to give a final white powder of dMMAO/SiO_2.

3.5 Polymerizations

3.5.1 Reactor 1: Autoclave Reactor

Propylene polymerization was performed in a 100-ml stainless steel autoclave reactor equipped with a magnetic stirrer. The required amounts of hexane (30 ml), TEA, catalyst (Al/Ti molar ratio = 167). The required amount of inorganic compounds was added into the reactor. Thereafter, it was frozen in liquid nitrogen to stop reaction between catalyst and cocatalyst and then evacuated to remove argon. The reaction was conducted at 60°C. Polymerization was started by continuous feeding of propylene at constant pressure of 60 psi for 1 h. The polymerization rate was determined by measuring the monomer consumption rate using a mass flow-meter. After the polymerization, the reaction was then terminated by venting the reactor and the product was washed with acidic methanol. The resulting polymer was filtered off and dried under vacuum at 60°C for 6 h.

3.5.2 Reactor 2: Glass Vessel Reactor

Propylene polymerization was performed in a 300 ml round-bottom glass reactor equipped with a magnetic stirrer. The required amounts of heptane (200 ml) and catalyst (0.095 mmol) were added into the reactor and then heated up to 30°C along with saturation of propylene at atmospheric pressure for 20 min. A desired amount of poisoning materials were introduced into the catalyst vessel for 1 min followed by the injection of TIBA (Al/Ti molar ratio: 30) to start polymerization. After undergoing of the reaction for 10 min, it was then terminated by venting the reactor and the product was washed with acidic ethanol and water for several times. The obtained polymer was then evaporated and dried under vacuum at 60°C for 6 h.

3.5.2 Reactor 3: Stopped-flow Reactor

The stopped-flow polymerization of propylene and estimation of the kinetic parameters were carried out according to the method reported previously [129,167-170]. The apparatus used for the stopped-flow polymerization is shown schematically in Figure 3.3. A and B are special glass vessels equipped with water jackets. The propylene polymerization was typically performed with catalyst (0.47 mmol Ti) and TIBA (14 mmol, Al/Ti molar ratio: 30) in heptane at 30°C for 0.1, 0.15 and 0.18s. The heptane slurry (100 ml) of the catalyst and a solution of TIBA in heptane (100 ml) saturated with propylene 1 atm, were placed in vessels A and B, respectively. All the vessels were stirred using magnetic stirrers to maintain a homogeneous state. Propylene concentration in *n*-heptane at 30°C was 0.6 mol L^{-1}. A 1000 mL flask containing ethanol (400 mL) and HCl (10 mL) were used as quenching agents. It was agitated vigorously to stop the polymerization instantaneously. MeOH, EtOH or 1-BuOH as poisoning materials were introduced into the catalyst vessel (A) for 1 min (Poisoning material/Ti molar ratio = 0.1). To start polymerization, they are forced to flow simultaneously through a Teflon tube (inner diameter 2 mm) from vessels A and B into flask C under a small pressure of nitrogen. The polymerization occurs in the Teflon tube from point X and subsequently quenched at point Y in flask C (a mixture of ethanol and HCl solution with vigorous agitation). The polymerization time can be controlled by adjusting the length of the Teflon tube from point X to Y.

Propagation rate constant k_p and active sites concentration [C*] were determined according to the following equations [171];

$$\overline{M}_n = M_0 \cdot \frac{k_p \cdot [\mathrm{M}] \cdot t}{1 + k_{tr} \cdot t} \qquad (1),$$

$$\mathrm{Y} = k_p \cdot [\mathrm{M}] \cdot [\mathrm{C}^*] \cdot t \qquad (2),$$

where $\overline{M}_n$, M_o, [M], t, k_{tr} and Y are the number-average molecular weight of the polymer, the molecular weight of the monomer, monomer concentration, polymerization time, transfer rate constant and polymer yield, respectively. Since the polymer yield is proportion to polymerization time up to ca. 0.2 s. Rearrangement of Equation (1) affords Equation (3), therefore, a plot of $1/\overline{P}_n$ versus $1/t$ should be linear.

$$\frac{1}{\overline{P}_n} = \frac{M_0}{\overline{M}_n} = \frac{k_{tr}}{k_p \cdot [M]} + \frac{1}{k_p \cdot [M]} \cdot \frac{1}{t} \qquad (3),$$

From the tangent and the intercept of the plot of $1/\overline{P}_n$ vs $1/t$, k_p and k_{tr} were obtained. When this value of k_p was substituted, [C*] can be calculated in Equation (2).

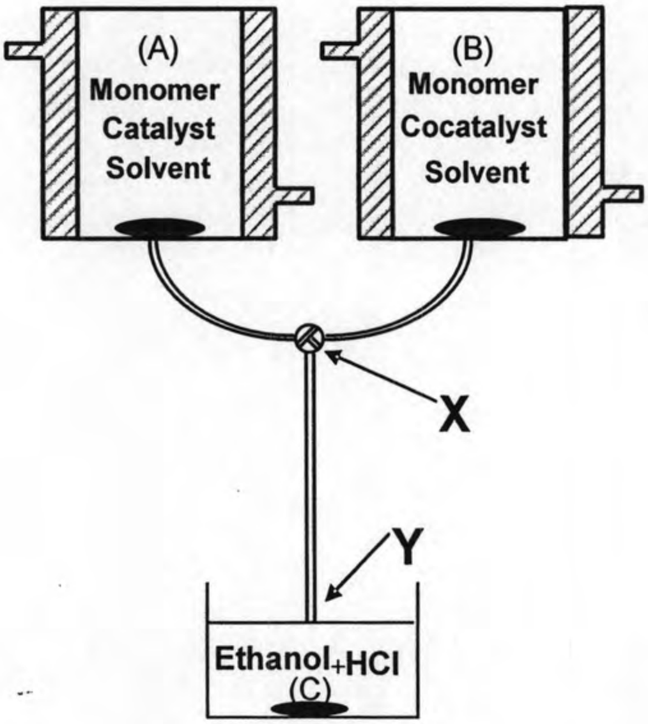

Figure 3.3 Schematic illustration of the stopped-flow apparatus.

3.6 Characterizations

3.6.1 N_2 Physisorption

Measurement of BET surface area, average pore diameter and pore size distribution of SiO_2-supported aluminoxanes were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system.

3.6.2 Scanning Electron Microscopy and Energy Dispersive X-ray Spectroscopy (SEM-EDX)

SEM and EDX were used to determine the morphologies and elemental distribution, respectively. The SEM of JEOL mode JSM-6400 was applied. The EDX was performed using Link Isis series 300 program.

3.6.3 Thermogravimetric Analysis (TGA)

TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 40 to 800°C at 10°C/min were used in the operation. The carrier gas was N_2 UHP.

3.6.4 Particle Size Distribution Analyzer (PSD)

The microsize particle was measured with a particle size distribution analyzer (PSD) on a Malvern Model Mastersizer S using laser light scattering technique.

3.6.5 Electron Spin Resonance (ESR)

The electron spin resonance (ESR) spectra of catalyst samples were recorded at ambient temperature, with the use of JEOL JES-FE1XG spectrometer under N_2 atmosphere. The values of the g factor were determined against the Mn^{2+} standard.

3.6.6 Soxhlet-Type Extractor

The stereoregularity of the obtained polymer was determined by measuring the isotactic index (I.I., wt% of polymer insoluble in boiling *n*-heptane) through Soxhlet extraction with *n*-heptane for 6 h.

3.6.7 ^{13}C Nuclear Magnetic Resonance (^{13}C NMR)

3.6.7.1 ^{13}C NMR 1

^{13}C NMR spectroscopy was used to determine the polymer microstructure. Sample solutions were prepared by dissolving 70 mg of polymer in 1,2,4-trichlorobenzene and benzene-d_6 for internal lock signal. The ^{13}C NMR spectra were taken at 110°C using BRUKER AVANCE II 400 operating at 100 MHz with an acquisition time of 1.5 s and a delay time of 4 s.

3.6.7.2 ^{13}C NMR 2

Stereoregularity of the polypropylene obtained was determined by ^{13}C NMR spectra (Varian Gemini 300 spectrometer) with diluted solutions in 1,1,2,2-tetrachoroethane-d_2 at 140 ^{o}C for internal lock and the central peak of 1,1,2,2-tetrachoroethane-d_2 (74.3 ppm) was used as an internal reference.

3.6.8 Differential Scanning Calorimetry (DSC)

Melting temperature (T_m) and crystallinity (X_c) of polymers were determined using differential scanning calorimetry, DSC (Perkin-Elmer DSC7). First, the sample was heated to 200°C at 10°C min^{-1}, which is well above the m.p., and maintained at this temperature for 10 min. Then, it was cooled to 30°C at 10°C min^{-1} to crystallize, followed by reheating at 10°C min^{-1}. The thermogram of each sample was recorded in the second heating run in order to remove the thermal history. The overall crystallinity was calculated from the heat of fusion values using the formula

$$X_c = H_m/H_p$$

where H_m is the enthalpy of the tested samples and H_p, the enthalpy of a totally crystalline PP, was assumed to be 209 J/g [172,173].

3.6.9 Gel Permeation Chromatography (GPC)

3.6.9.1 GPC 1

Gel permeation chromatography (GPC) of polymers was performed on a three Shodex AT type columns (AT-803, AT-805 and AT-807) for determining the molecular weight (M_W) and molecular weight distribution (MWD). The columns were calibrated with standard narrow m Molecular weight and molecular weight distribution of the polypropylene obtained in this study were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (Tosoh TSK-GEL G3000HHR and TSK-GEL G5000HHR) at 140°C using *o*-dichlorobenzene (ODCB) as a solvent.

3.6.9.2 GPC 2

Molecular weight and molecular weight distribution of the polypropylene obtained were determined by gel permeation chromatography (GPC, Senshu SSC-7100) with polystyrene gel columns (Tosoh TSK-GEL G3000HHR and TSK-GEL G5000HHR) at 140°C using *o*-dichlorobenzene (ODCB) as a solvent.