

## CHAPTER III

### EXPERIMENT

#### 3.1 Chemicals

The chemicals used in these experiments of the investigation were specified as follows :

1. Argon gas (Ultra High Purity 99.999%) was purchased from Thai Industrial Gas Co., Ltd. (TIG)

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

3. Bis(butylcyclopentadienyl)zirconium dichloride ((n-BuCp)<sub>2</sub>ZrCl<sub>2</sub>, 97.0%) was supplied from Aldrich chemical Company, Inc.

4. Bis(cyclopentadienyl)titanium dichloride (Cp<sub>2</sub>TiCl<sub>2</sub>, 99.0%) was purchased from Strem Chemical.

5. Bis(cyclopentadienyl)zirconium dichloride (Cp<sub>2</sub>ZrCl<sub>2</sub>) was obtained from Japan.

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

7. Cyclopentadienyl titanium trichloride (CpTiCl<sub>3</sub>) was purchased from Strem Chemical.

8. Ethylene gas (polymerization grade) was devoted from National Petrochemical Co., Ltd., Thailand.

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

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

11. Methyaluminoxane (MAO) 2.534 M in toluene was donated from Tosoh Akso, Japan.

12. racemic-Ethylenebis(indenyl)zirconium dichloride (rac-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub>) was obtained from Aldrich chemical Company, Inc.

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

14. Toluene was donate from Exxon Chemical Ltd., Thailand.

15. Trichloro(pentamethyl cyclopentadienyl) titanium ( $\text{Cp}^*\text{TiCl}_3$ , 97.0%) was purchased from Aldrich chemical Company, Inc.

16. Trimethyl(pentamethyl cyclopentadienyl) titanium ( $\text{Cp}^*\text{TiMe}_3$ , 97.0%) was manufactured from Alfa Aesca.

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

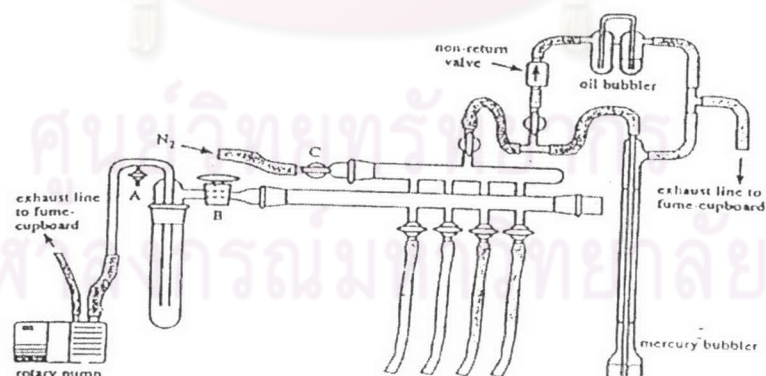
## 3.2 Equipments

### 3.2.1 Equipment for handling air-sensitive compounds

Since the most of reagents and catalysts were very sensitive to the oxygen and moisture therefore special techniques were taken in the handling of reagents and for loading the catalyst into the reactor. Such equipment utilized for this purpose are as follows :

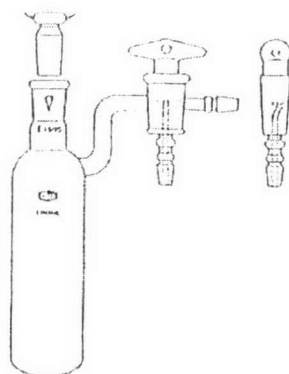
(a) Glove box (Vacuum Atmospheres) with oxygen and moisture analyzer for transferring solid reagents under inert atmosphere and for storing air-sensitive reagents. The oxygen and moisture levels are normally below 2 ppm inside the glove box.

(b) Schlenk line included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 3.1.



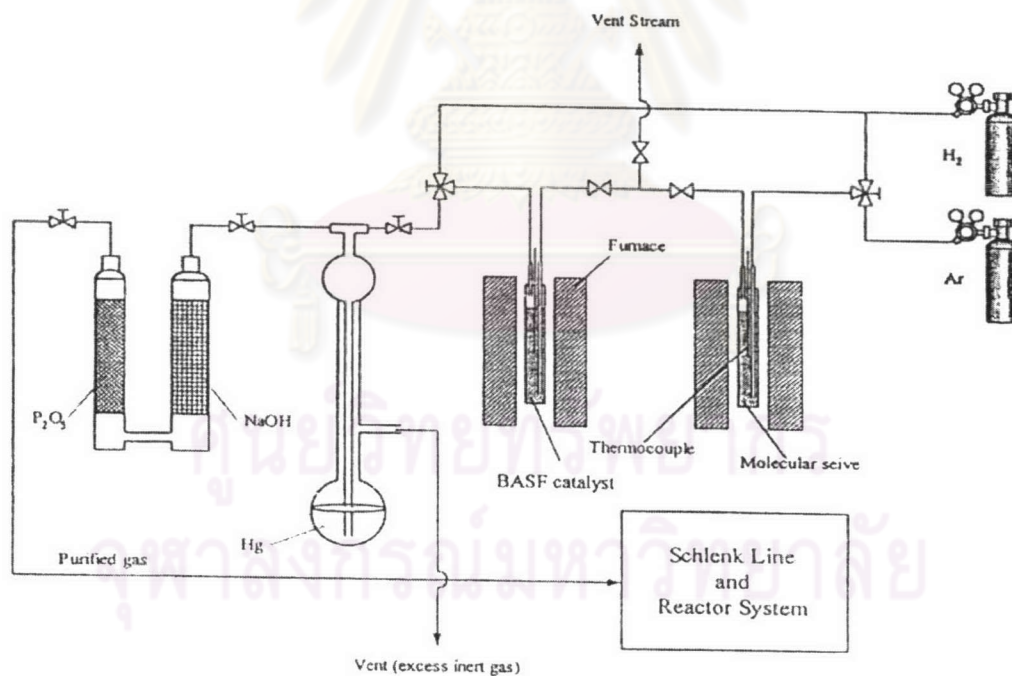
**Figure 3.1.** Schlenk line

(c) Schlenk tube for keeping reagents under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line. Schlenk tube is a tube with a ground joint and side arm which was three way glass valve as shown in Figure 3.2.



**Figure 3.2.** Schlenk tube

(d) The inert gas (argon) was pass through columns of oxygen trap (BASF catalyst, R3-11G), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentaoxide ( $P_2O_5$ ) for purifying ultra high purity argon before use in Schlenk line and solvent distillation column. The inert gas supply system is shown in Figure 3.3.



**Figure 3.3.** Inert gas supply system

(e) The vacuum pump model 195 from Labconco Coporation 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 Polymerization procedure

#### 3.3.1 Material preparation

Since the solvents were of commercial grade, there might be some undesirable impurities; especially water, which have to be removed before use. Therefore solvents are refluxed in the presence of Na/benzophenone and the distilled under argon atmosphere and kept in Schlenk tubes.

Ethylene is polymerization grade which purified by passing through a column of LABCLEAR™ gas filter. The ultra high purity argon was further purified by pass through molecular sieve 3A, BASF catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P<sub>2</sub>O<sub>5</sub>) to remove traces of oxygen and moisture.

#### 3.3.2 Ethylene and Norbornene copolymerization

Ethylene and norbornene copolymerization in the slurry phase was carried out in 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in an oven at 110°C for 30 minutes and purged with argon for 5 times in a glove box before use in copolymerization. Toluene (the total volume of mixture solution was 30 ml) and desired amount of rac-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub> and MAO were mixed and stirred for 5 minutes at room temperature. After that, the mixture of catalyst and MAO was introduced into the reactor outside a glove box. The loaded reactor was then frozen in liquid nitrogen to stop the reaction for 15 minutes and then the autoclave was degassed. The reactor immersed into the water bath controlled to the desired reaction temperature and the polymerization was started by feeding ethylene gas (total pressure 50 psi) until the consumption of ethylene 6 psi was observed from the pressure gauge. A small amount of ethylene was used to avoid the mass transfer effect and increase the homogeneity of polymer. After the polymerization reaction was stopped, the reaction solution was terminated by an addition of acidic methanol. The precipitated polymer was washed with methanol several times and dried under vacuum. Ethylene and norbornene copolymerization procedure and a schematic diagram of the system are displayed in Figure 3.4 and 3.5, respectively.

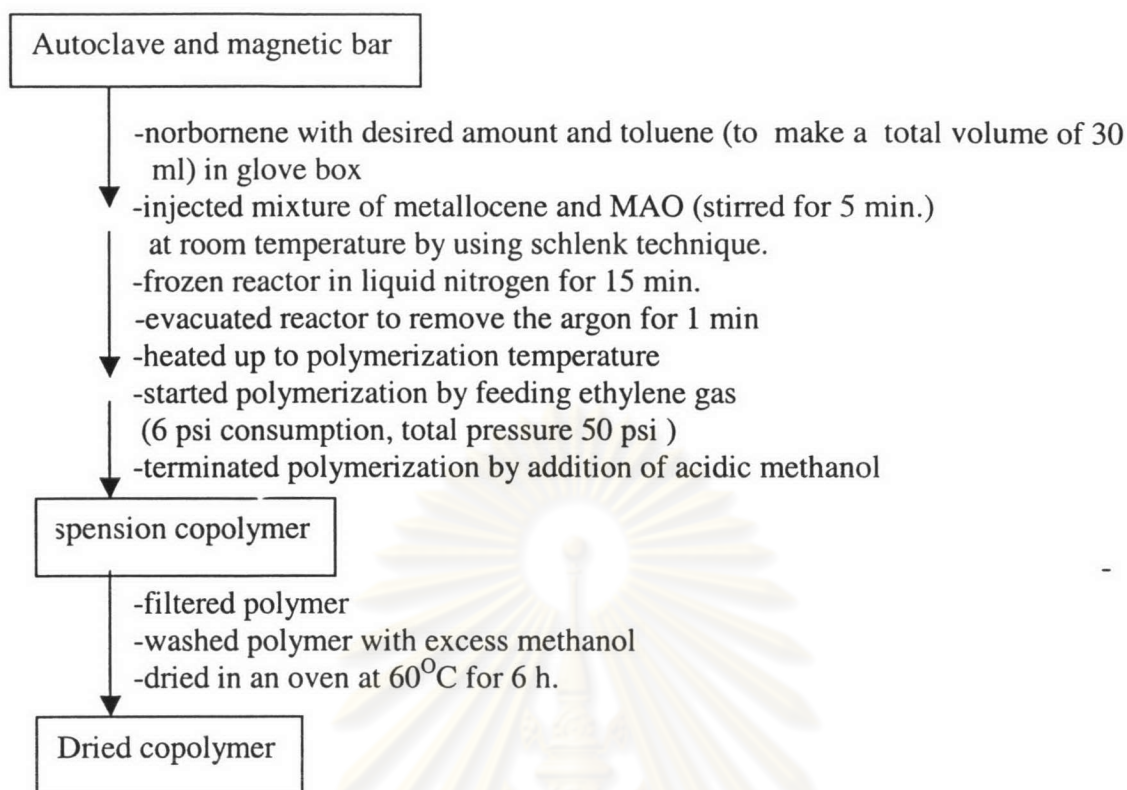


Figure 3.4. Ethylene and norbornene Copolymerization Procedure

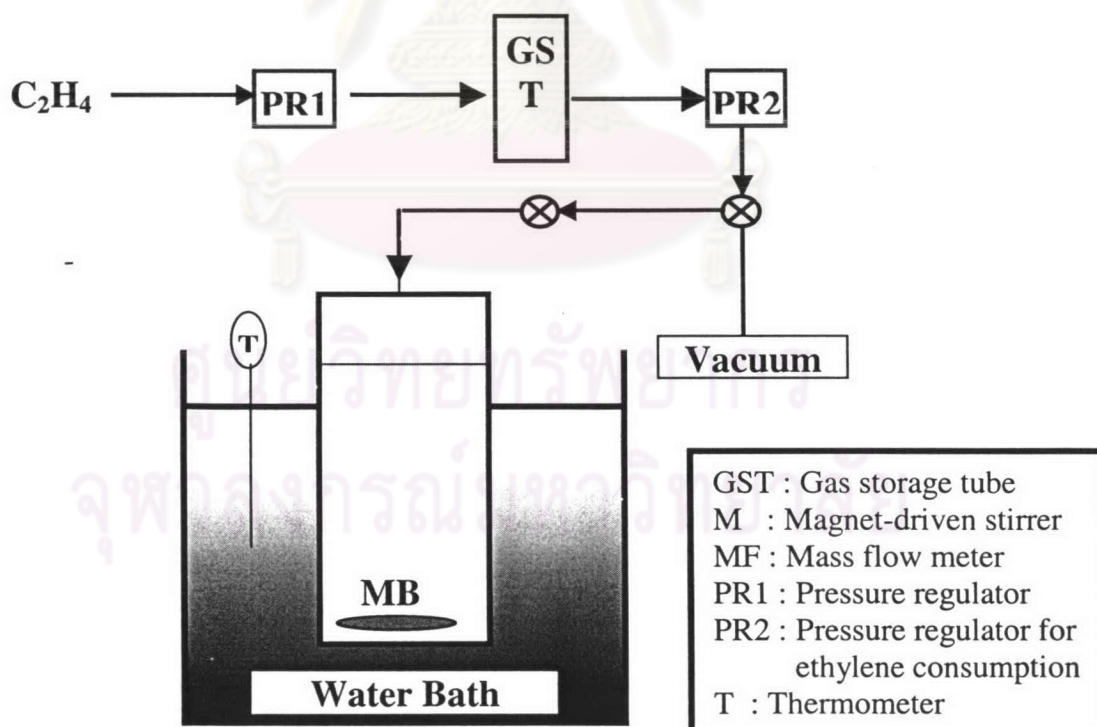


Fig 3.5. Schematic diagram of reactor system in slurry phase polymerization

The various effects on the ethylene and norbornene copolymerization with metallocene catalyst system were investigated. The effects of copolymerization on production of ethylene and norbornene copolymer were systematically varied as follows :

### **3.3.2.1 The effect of cocatalyst and catalyst molar ratio ( $Al_{MAO}/Zr$ )**

The Al/Zr molar ratios were varied from 750 to 4000. The concentration of rac-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub> was fixed  $5.0 \times 10^{-5}$  M and the consumption of ethylene was fixed at 6 psi. The polymerization temperature and norbornene concentration were kept constant at 40°C and 0.1 M, respectively.

### **3.3.2.2 The effect of catalyst concentration**

The concentrations of rac-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub> catalyst were investigated at  $3.3 \times 10^{-5}$  M to  $10.0 \times 10^{-5}$  M. The consumption of ethylene, norbornene concentration and polymerization temperature were operated constantly at 6 psi, 0.1 M and 40°C, respectively whereas the suitable Al/Zr molar ratio from section 3.3.2.1 was kept constant.

### **3.3.2.3 The effect of polymerization temperature**

The ethylene and norbornene copolymerization was further studied by varying the polymerization temperature from 30°C to 90°C using the suitable conditions selected from section 3.3.2.2.

### **3.3.2.4 The effect of type of metallocene catalyst**

The ethylene polymerization and ethylene/norbornene copolymerization which using seven different metallocene catalyst such as rac-Et[Ind]<sub>2</sub>ZrCl<sub>2</sub>, (n-BuCp)<sub>2</sub>ZrCl<sub>2</sub>, Cp<sub>2</sub>ZrCl<sub>2</sub>, Cp<sub>2</sub>TiCl<sub>2</sub>, CpTiCl<sub>3</sub>, Cp\*TiCl<sub>3</sub> and Cp\*TiMe<sub>3</sub> were investigated at the similar polymerization conditions. The conditions of polymerization were used from the result of section 3.3.2.1 to 3.3.2.3.

### 3.3.2.5 *The effect of norbornene concentration*

The concentrations of norbornene were studied at 0.03 M to 0.2 M and compared the catalytic activity between ethylene and norbornene copolymerization and homopolymerization of ethylene. The conditions of polymerization were selected from the result of section 3.3.2.1 to 3.3.2.4.

### 3.3.2.6 *The effect of polymerization time*

The polymerization time of ethylene and norbornene copolymerization were investigated from 30 min to 120 min with 0.3 M of norbornene in different types of solvent such as aromatic (toluene and xylene) and aliphatic solvents (1-hexane, 1-heptane and 1-decane). The conditions of polymerization were selected from the result of section 3.3.2.1 to 3.3.2.4.

**Remarkd :** In the same of experimental set, the catalyst were identical.

## 3.4 Polymer Characterization

### 3.4.1 Scanning Electron Microscope (SEM)

Scanning Electron Microscope (SEM) was the effective method to investigat polymer morphology. The term of morphology was referred to shape, texture or form of polymers. The morphology of catalyst and polymers was examined by scanning electron microscopy (SEM) with a JSM-640 Scanning Microscope, Microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University using a camera and a Polaroid film. The polymer samples were coated with a thin layer of gold particles by ion sputtering before they were placed in the specimen chamber of the SEM.

### 3.4.2 Differential Scanning Calorimetry (DSC)

The melting temperature and glass transition temperature of the copolymers were determined with a Perkin-Elmer DSC 7 at Central Instrument Facility Faculty of Science, Mahidol University. The analyses were performed at the heating rate of 10°C/min in the temperature range 0-150°C. The heating cycle was

run twice. In the first scan, samples were heated up and then cooled down to 0°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. Percent crystallinity was computed from enthalpies of melting by Equation 3.1, using the reliable value of Wunderlich.

$$\chi (\%) = (\Delta H_m / \Delta H_m^\circ) \times 100 \quad (3.1)$$

Where ( $\Delta H_m$ ) is the heat of fusion of sample and ( $\Delta H_m^\circ$ ) is the heat of fusion of 100% crystalline polyethylene [290 J/g] (Ottani and Porter, 1991).

### 3.4.3 $^{13}\text{C}$ -Nuclear Magnetic Resonance ( $^{13}\text{C}$ -NMR)

$^{13}\text{C}$ -NMR spectroscopy was widely used to determine comonomer incorporation and polymer structure. Comparison of the positions of peak in the  $^{13}\text{C}$ -NMR spectrum of polymer sample with characteristic led to identification of the sequence of the comonomer incorporation. Sample solutions were prepared in *o*-dichlorobenzene and benzene- $d_6$  (20 vol%) for internal lock single. The  $^{13}\text{C}$ -NMR spectra were obtained at 110°C using JEOL JNM-A500 operating at 125 MHz (at the Scientific Technological Research Equipment Centre, Chulalongkorn University).

### 3.4.4 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 the 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 polyethylene products.



### 3.4.5 Thermal Gravimetric Analysis (TGA)

The weight loss pattern of the samples during heating up was analyzed by Shimadzu TGA model 50. The sample was loaded in a platinum pan located in a furnace. The purging gas were nitrogen with flow rate 30 ml/min and air with flow rate 100 ml/min. The furnace temperature was programmed to rise from room temperature to 600°C at a constant rate of 10°C/min. The data were displayed and recorded using a microcomputer.



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