

## CHAPTER III EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Catalyst

Bis(cyclopentadienyl) zirconium dichloride ( $\text{Cp}_2\text{ZrCl}_2$ )(Figure 3.1 (a)) catalyst was purchased from Boulder Scientific Company and used without further purification.

#### 3.1.2 Cocatalysts

Tris(pentafluorophenyl) borane ( $\text{B}(\text{C}_6\text{F}_5)_3$ )(Figure 3.1 (b)) was obtained from Boulder Scientific Company.

Trimethylaluminum(TMA) was obtained from Nippon Aluminum Alkyls Ltd., as a 2000 mmol of Al/I solution in toluene.

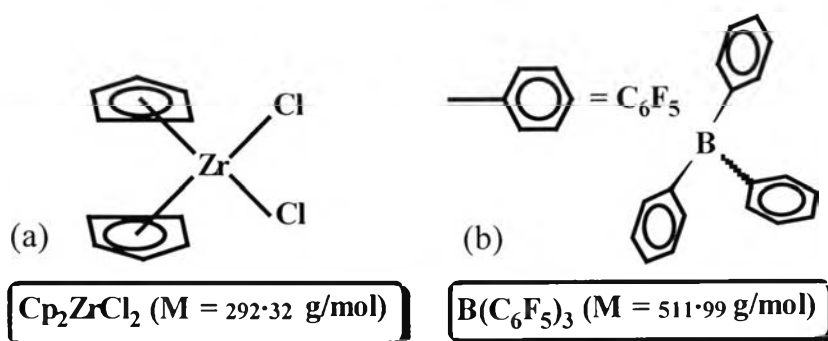


Figure 3.1 Structures of  $\text{Cp}_2\text{ZrCl}_2$  (a) and  $\text{B}(\text{C}_6\text{F}_5)_3$  (b).

#### 3.1.3 Monomer

Polymerized grade ethylene gas was provided by the National Petrochemical Public Company Limited. The gas was passed through

oxygen/moisture trap (Matheson gas products, model 6427-4) to remove residual traces of oxygen and moisture before entering the reactor.

### 3.1.4 Solvent

Toluene (AR-grade) was purchased from Labscan Company Limited. It was further purified by refluxing in sodium/benzophenone for approximately 2 days until a dark blue color was obtained followed by distillation under an inert atmosphere of nitrogen.

Table 3.1 gives details of all the reagents used in this work.

Table 3.1 Reagents used in experiments.

Name of Chemicals	Formula/Abbr.	Grade	Source
Acetone	CH <sub>3</sub> COCH <sub>3</sub>	Commercial	Labscan
Benzophenone	(C <sub>6</sub> H <sub>5</sub> ) <sub>2</sub> CO	A.R	Labscan
Ethylene	C <sub>2</sub> H <sub>4</sub>	Polymerized gr.	NPC
Hydrochloric Acid	HCl	37%	Merck
Methanol	CH <sub>3</sub> OH	Commercial	Labscan
Nitrogen	N <sub>2</sub>	UHP (99.999%)	TIG
Sodium	Na	G.R	Fluka
Toluene	CH <sub>3</sub> C <sub>6</sub> H <sub>5</sub>	A.R	Labscan
Trimethylaluminum	TMA	2000 mmolAl/l in toluene	Nippon Aluminum Alkyls Ltd.,
Tris(pentafluorophenyl) borane	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub>	Research	Boulder Sci.
Zirconocene Dichloride	Cp <sub>2</sub> ZrCl <sub>2</sub>	Research	Boulder Sci.

## 3.2 Equipment

### 3.2.1 *The constant pressure reactor system*

The reaction was carried out in a 300 ml Parr reactor(Parr Instrument Company), equipped with a pitched-blade turbine impeller with a speed controller, external heating jacket, thermowell, and pressure transducer. The impeller speed, outer jacket temperature, and internal reactor temperature and pressure are digitally displayed on the front panel.

### 3.2.2 *The glove-box*

Since the catalyst systems used in this study are highly air-sensitive, all sample preparations were carried out in an air-tight glove-box purged constantly with purified nitrogen.

## 3.3 Methodology

### 3.3.1 *Ethylene polymerization*

A schematic diagram of the reactor system used for ethylene polymerization is shown in Figure 3.2. The reactor is a 300 ml stainless steel reactor equipped with a temperature controller and stirrer. To start the experiment, the reactor was first heated up to 120 °C, evacuated and flushed with nitrogen several times. The nitrogen gas was then allowed to flow into the reactor after passing through moisture and oxygen trap. After the purging was complete, the reactor was cooled down to room temperature. Next a predetermined amount of toluene was fed into the reactor from the transfer vessel with nitrogen overpressure and this was followed by the addition of cocatalyst. The reactor content was continuously stirred following the addition of toluene. The temperature was controlled with PID temperature controller to the desired temperature. After that ethylene gas was fed into the

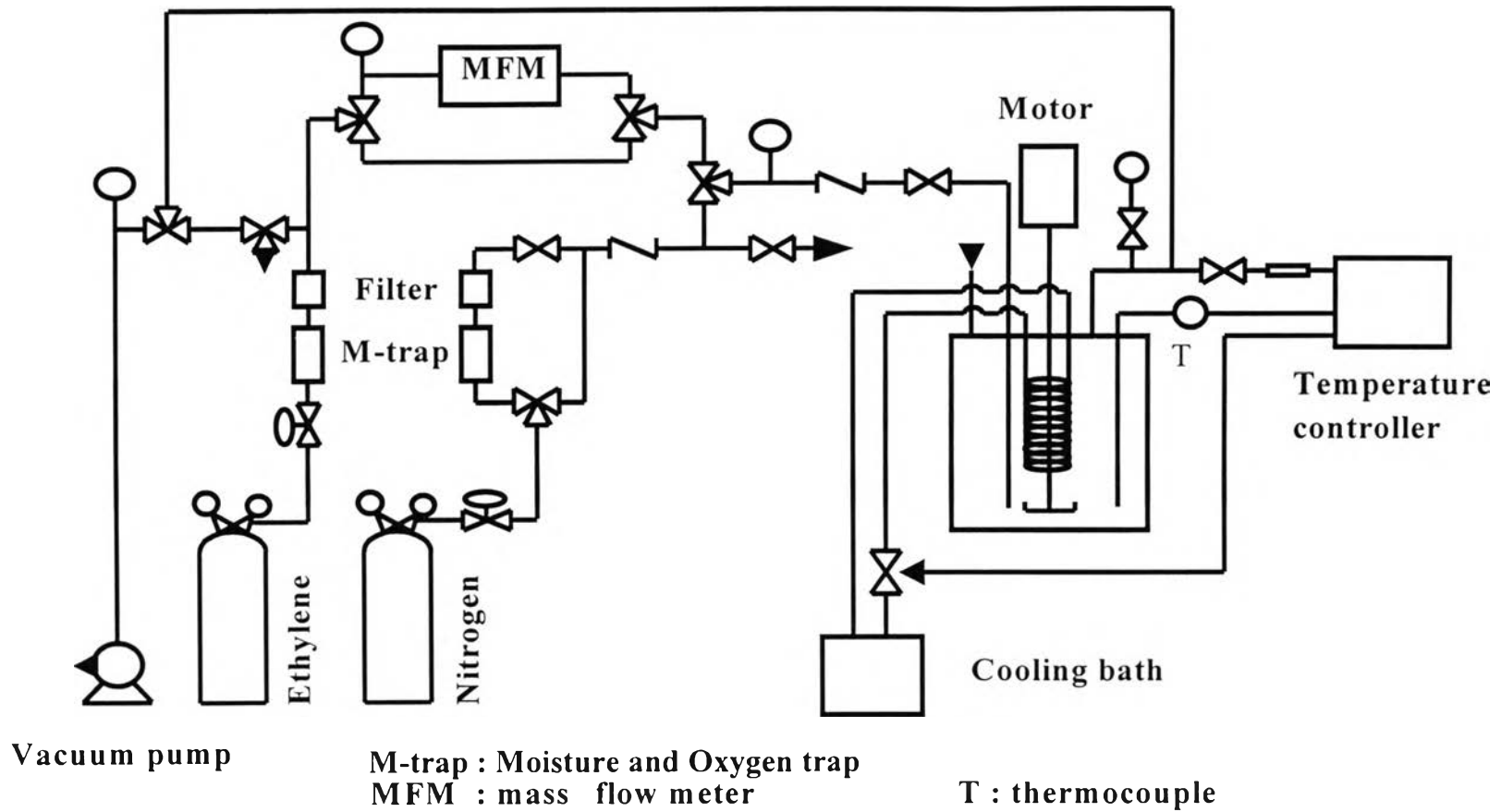


Figure 3.2 Schematic of experimental polymerization setup.

reactor after passing through a moisture and oxygen trap until a pressure of 2 atm was obtained at which point the reaction medium was saturated. Then the polymerization was started by injecting the catalyst/toluene solution into the reactor with pressure injection. Ethylene was fed into the reactor for 1 hour of reaction time in a semi-batch mode. This semi-batch operation replenished the consumed amount, thereby maintaining a constant polymerization pressure by continuous gaseous monomer feeding with no gas vent or polymer discharge during reaction. This feature also means that under quasi-steady state, rate of accumulation of gas in the reactor is negligible if a constant pressure is maintained, the rate of monomer flow into the reactor is equal to the rate of monomer consumption by reaction. The consumption of ethylene was followed with a mass-flow meter (Cole-Parmer Model 33115-60).

After a reaction time of 1 hour, the polymerization was quenched by stopping the ethylene supply, venting the reactor, and injecting an amount of methanol acidified with 2.5 vol % HCl to stop the reaction. The polymer product was then taken out, filtered, washed several times with methanol, and dried in a vacuum oven at 50 °C for 12 hours. The product was weighed to give the productivity of the polymerization reaction.

