CHAPTER III
EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst

Bis(cyclopentadienyl) zirconium dichloride (Cp_2ZrCl_2) catalyst was purchased from Boulder Scientific Company and used without further purification.

3.1.2 Cocatalyst

Tris(pentafluorophenyl) borane ($B(C_6F_5)_3$) was obtained from Boulder Scientific Company.

Triethylaluminum (TEA) was provided by Thai Polyethylene Co. Ltd. as a 1000 mmol of Al/L solution in toluene.

Tributylaluminum (TBA) was purchased from Aldrich as a 1 M of Al solution in toluene.

3.1.3 Monomer

Polymerization-grade ethylene gas was provided by National Petrochemical Public Company Limited. 99.99% high purity nitrogen gas from Thai Industrial Gas.

Both were used after passing through oxygen/moisture trap (Matheson gas products, model 6427-4) to remove residual traces of oxygen and moisture to below 20ppb level before entering the reactor.

3.1.4 Solvent

Toluene (AR-grade) was purchased from J. T. Baker Company Limited. It was further purified as described in Section 3.3.1.

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

Table 3.1 Reagents used in this study.

Name of Chemicals	**Formula**	**Grade**	**Source**
Sodium metal	Na	G. R.	Fluka
Benzophenone	$(C_6H_5)CO$	A. R.	Labscan
Nitrogen	N_2	99.99% HP	TIG
Toluene	$CH_3C_6H_5$	A. R.	J. T. Baker
Methanol	CH_3OH	Commercial	Labscan
Acetone	CH_3COCH_3	Commercial	Labscan
Ethylene	C_2H_4	Poly^n grade	NPC
Triethylaluminum	$Al(CH_2CH_3)_3$	1000 mmol Al/l in toluene	TPE
Tributylaluminum	$Al((CH_2)_3CH_3)_3$	1 M Al in toluene	Aldrich
Zirconocene Dichloride	Cp_2ZrCl_2	Research	Boulder Sci.
Tris (pentafluorophenyl) borane	$B(C_6F_5)_3$	Research	Boulder Sci.

3.2 Equipment

3.2.1 The constant pressure reactor system

The polymerization was carried out in a 300 ml Parr reactor (Parr Instrument Company), equipped with a pitch-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 are highly air-sensitive, all sample preparations were carried out in an air-tight glove-box (Labconco Protector Glove Box Model 50800) purged constantly with purified nitrogen.

3.3 Methodology

3.3.1 Solvent Purification

Toluene used as the solvent was purified by pre-drying the solvent with molecular sieves 4A prior to distill in the presence of sodium metal and reflux with stirring under N_2 gas until the sodium was molten and shiny. A small quantity of benzophenone was added quickly in portions under a slow flow of N_2. The colour of the ketyl took several minutes to develop so some time was allowed to elapse before more benzophenone was added .

Benzophenone was used here as an indicator. It shows a blue or even dark blue colour when there is no moisture or other impurity in the distilled system. It turns purple if there is too much oxygen, moisture or other impurity during the distillation. The use of UHP (99.99%) N_2 gas was nescessary to obtain the high-purity solvent.

Once the still was under N_2 for some time and the dark blue colour of the ketyl persisted (additional of benzophenone was needed from time to time), then about ¾ of the toluene was distilled off under N_2 into a dry vessel. The still was then cooled to room temperature, more toluene was added to the still and the process restarted all over again. From this process, 3-5 lots of toluene could be collected with about the same purity level before the distillation was stopped by quenching the still to room temperature before methanol was added, the ketyl would be consumed first followed by the sodium metal remaining.

3.3.2 Ethylene Polymerization

A schematic diagram of the reactor system used for ethylene polymerization is shown in Figure 3.1 The reactor was 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, nitrogen gas was allowed to flow into the reactor while heating, the reactor was then evacuated and flushed with nitrogen again for several times. After the purging was complete, the reactor was cooled down to room temperature.

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 catalyst. The reactor content was continuously stirred following the addion of toluene. The temperature was controlled with PID temperature controller to the desired temperature. After that ethylene gas was fed into the reactor after passing through a moisture and oxygen trap until the desired pressure was obtained at which point the reaction medium was saturated. Then the polymerization was started by injecting the cocatalyst $B(C_6F_5)_3$/toluene solution into the reactor with pressure injection followed by the aluminum/toluene. Ethylene was fed into the reactor for 1 hour of reaction time in a semi-batch mode. This semi-batch operation replenished the

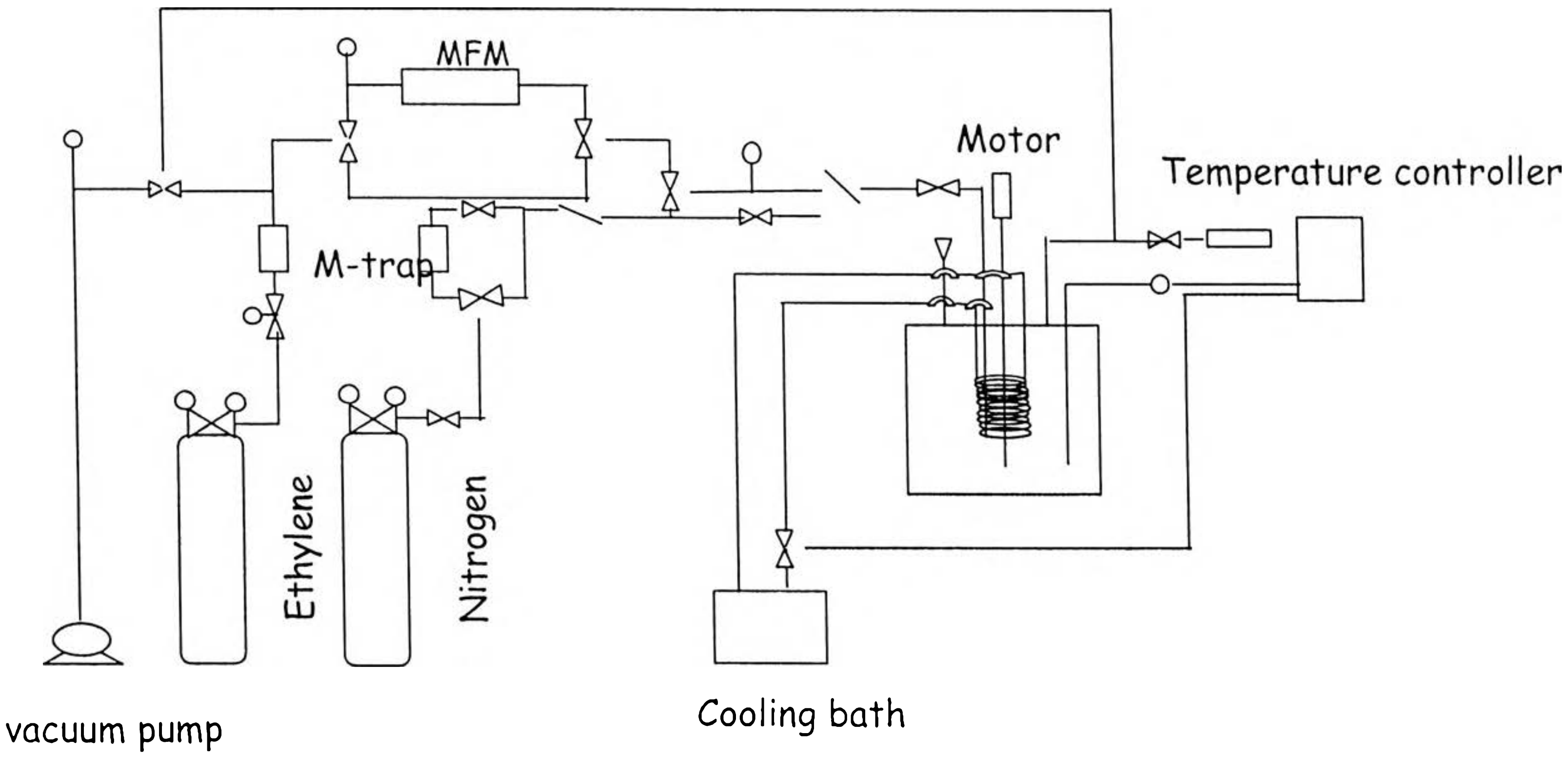

Figure 3..1 Schematic of experimental polymerization setup

consumed amount, thereby maintaining a constant polymerization pressure by contineous gaseous monomer feeding with no gas vent or polymer discharged during reaction. This feature also means that, under this 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 by a mass-flow meter (Aalborg Model GFM 37/47).

After a reaction time of 1 hour, the polymerization was terminated by stopping the ethylene supply, venting the reactor and injecting acidic methanol to stop the reaction The polyethylene product was then taken out, filtered, washed several times with methanol, and dried in an oven at 80 °C for 12 hours. It was finally weighed to calculate the productivity of the reaction.

3.3.3 Characterization of Polyethylene Products

3.3.3.1 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution of the polyethylene products were determined using a Waters high-temperature 150-C plus GPC instrument equipped with three Waters Ultrastyragel columns in series at 140 °C. The columns have exclusion limits for polystyrene 10^4, 10^5 and 10^6 °A pore size. The solvent, o-dichlorobenzene, was applied at a flow rate of 1.0 cm^3/min. The columns were calibrated with narrow molecular weight distribution polystyrene samples.

3.3.3.2 Differential scanning calorimetry (DSC)

The percent crystallinity in the polymer was determined using a Perkin-Elmer DSC7 calorimeter. Each sample was heated from 50 °C to 160 °C with a heating rate of 20 °C/min and was then cooled down to 50 °C and again reheated at the same rate. The values of melting point (T_m) were obtained in the second scan.

The crystallinity was calculated from equation 3.1 below :

$$\% X = (\Delta H_f / (\Delta H_f^*) \times 100 \qquad \_\_\_\_(3.1)$$

The endothermic heat of fusion peak, ΔH_f, was obtained from the DSC thermogram (Figure 3.2). The area under this peak is proportional to the percent crystallinity of the sample so it is important to know the area which corresponds to a 'hypothetical' 100% crystalline polymer and the heat of fusion of perfectly crystalline polyethylene, ΔH_f^*, is 286 J/g (Gray, 1970).

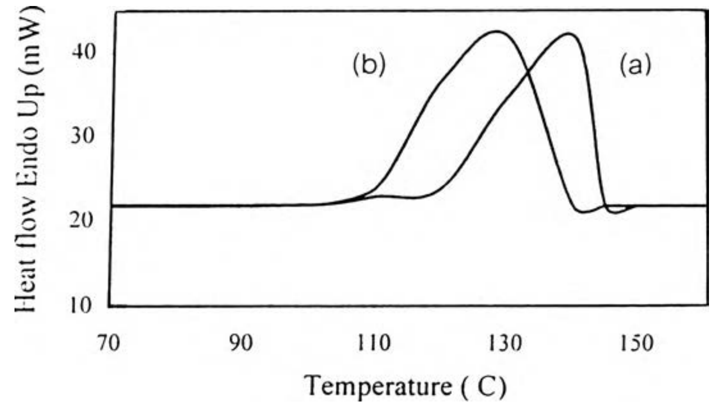

Figure 3.2 The DSC thermograms of (a) first and (b) second scans of metallocene polyethylene

3.3.3.3 Wide angle X-ray diffraction (WAXD)

Crystallinity was also obtained from WAXD (D/MAX-2000 series of Riguku/X-ray Diffractometer system). The experiment was performed in the range of 2-40 degree with scanning speed of 10 deg./min and scanning step 0.02 deg.

The degree of crystallinity was calculated from the equation 3.2 below :

$$X = (A_1 + A_2) / (A_1 + A_2 + A_3) \qquad \text{\_\_\_\_\_\_\_\_} (3.2)$$

where $A_1 + A_2$ is the crystalline peak area and $A_1 + A_2 + A_3$ is the total area. These values were obtained from the polyethylene X-ray diffraction pattern (Figure 3.3), where the sharp peaks represent the crystalline areas and the broad peak represents the amorphous area.

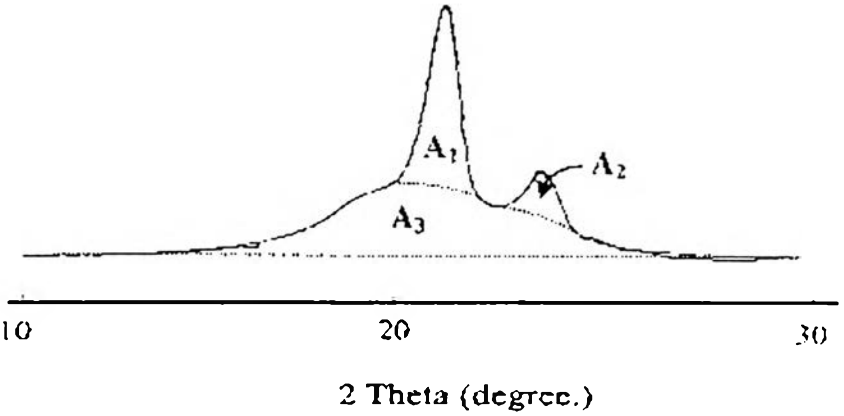

Figure 3.3 X-ray diffraction pattern

3.3.3.4 Scanning electron microscope (SEM)

The morphology of polyethylene products was examined by using SEM model JOEL 520 at a voltage of 10 kV and 3500 × magnification.