

CHAPTER III

EXPERIMENTAL

3.1 Materials

3.1.1 Catalyst

Bis(cyclopentadienyl)zirconocene dichloride (Cp_2ZrCl_2) catalyst was purchased from Fluka and used without further purification.

3.1.2 Cocatalysts

Tris(pentafluorophenyl)borane ($\text{B}(\text{C}_6\text{F}_5)_3$) was obtained from Albemarle.

Triethylaluminum (TEA) was provided by Thai Polyethylene Co. Ltd. as a 1000 mmol of Al/L 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 was 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 20 ppm 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 ₆ H ₅)CO	A.R.	Labscan
Nitrogen	N ₂	99.99% HP	TIG
Toluene	CH ₃ C ₆ H ₅	A.R	J.T. Baker
Methanol	CH ₃ OH	Commercial	Labscan
Acetone	CH ₃ COCH ₃	Commercial	Labscan
Ethylene	C ₂ H ₄	Poly ⁿ grade	NPC
Triethylaluminum	Al(CH ₂ CH ₃) ₃	1000 mmol Al-1 in toluene	TPE
Zirconocene Dichloride	Cp ₂ ZrCl ₂	Research	Fluka
Tris (pentafluorophenyl) borane	B(C ₆ F ₅) ₃	Research	Albemarle

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 displayed on the front panel.

3.2.2 The Glove-box

Since the catalyst systems used are highly air-sensitive, all sample preparations were conducted 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

A schematic diagram of the solvent purification equipment is shown in Figure 3.1. Toluene used as the solvent was purified by pre-drying the solvent with molecular sieves 4A prior to distillation 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 impurities in the distilled system. It turns purple if there is too much oxygen, moisture or other impurities during the distillation step. The use of UHP (99.99%) N_2 gas was necessary 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 3/4 of 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 controlled with about the same purity level before the distillation step 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.

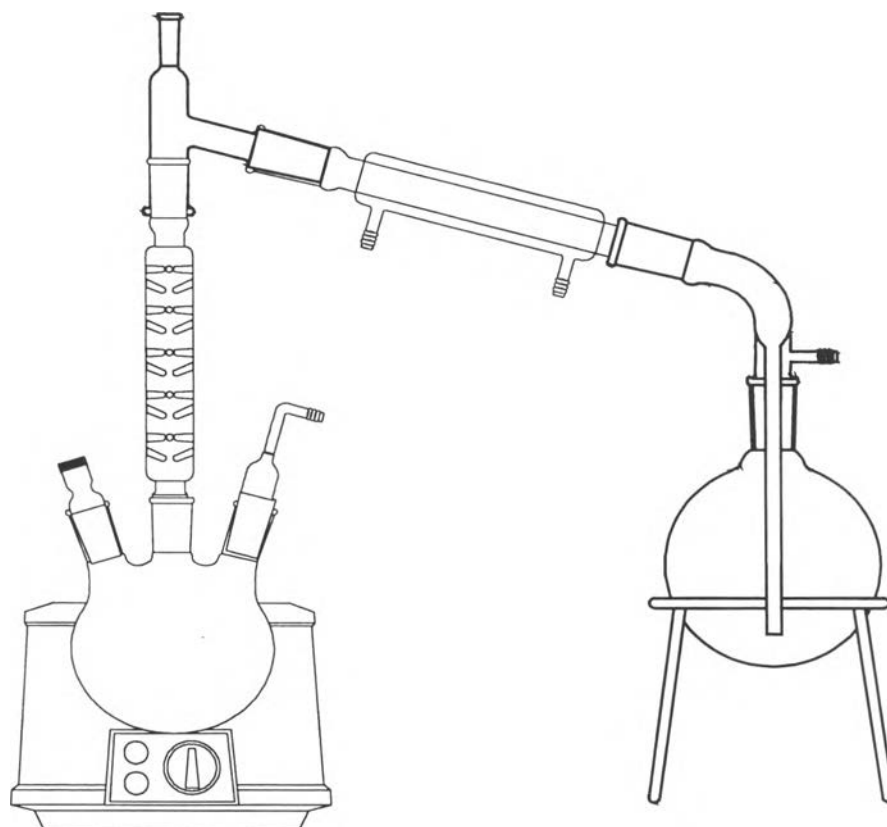


Figure 3.1 The equipment for solvent purification.

3.3.2 Ethylene Polymerization

A schematic diagram of the reactor system used for ethylene polymerization is shown in Figure 3.2. 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 catalyst dissolved in toluene and triethylaluminum in toluene solution were premixed under nitrogen atmosphere and then was injected into the reactor from the transfer vessel with nitrogen over pressure. The premixed solution was saturated with an atmospheric pressure of ethylene. The reactor content was continuously stirred followed by the addition of cocatalyst $B(C_6F_5)_3$ in toluene solution. 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 monomer feeding with no gas vent or polymer discharge during reaction. This feature also means that under this quasi-steady state the 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 monitored by a mass-flow meter (Aalborg Model GFM 37/47). After the specified polymerization time of 1 h, methanol was injected into the reactor to terminate the polymerization. The polymer was filtrated, washed several times with methanol, dried at 40°C for 24 hrs and weighed. The productivity of the reaction was calculated by the following equation.

$$\begin{aligned} &\text{Productivity (KgPE/mol-Zr*atm*h)} \\ &= \frac{[\text{Polyethylene product (kg)}]}{[\text{Amount of Catalyst(mol-Zr)}][\text{Ethylene pressure (atm)}][\text{Time (min)}]} \end{aligned} \quad (3.1)$$

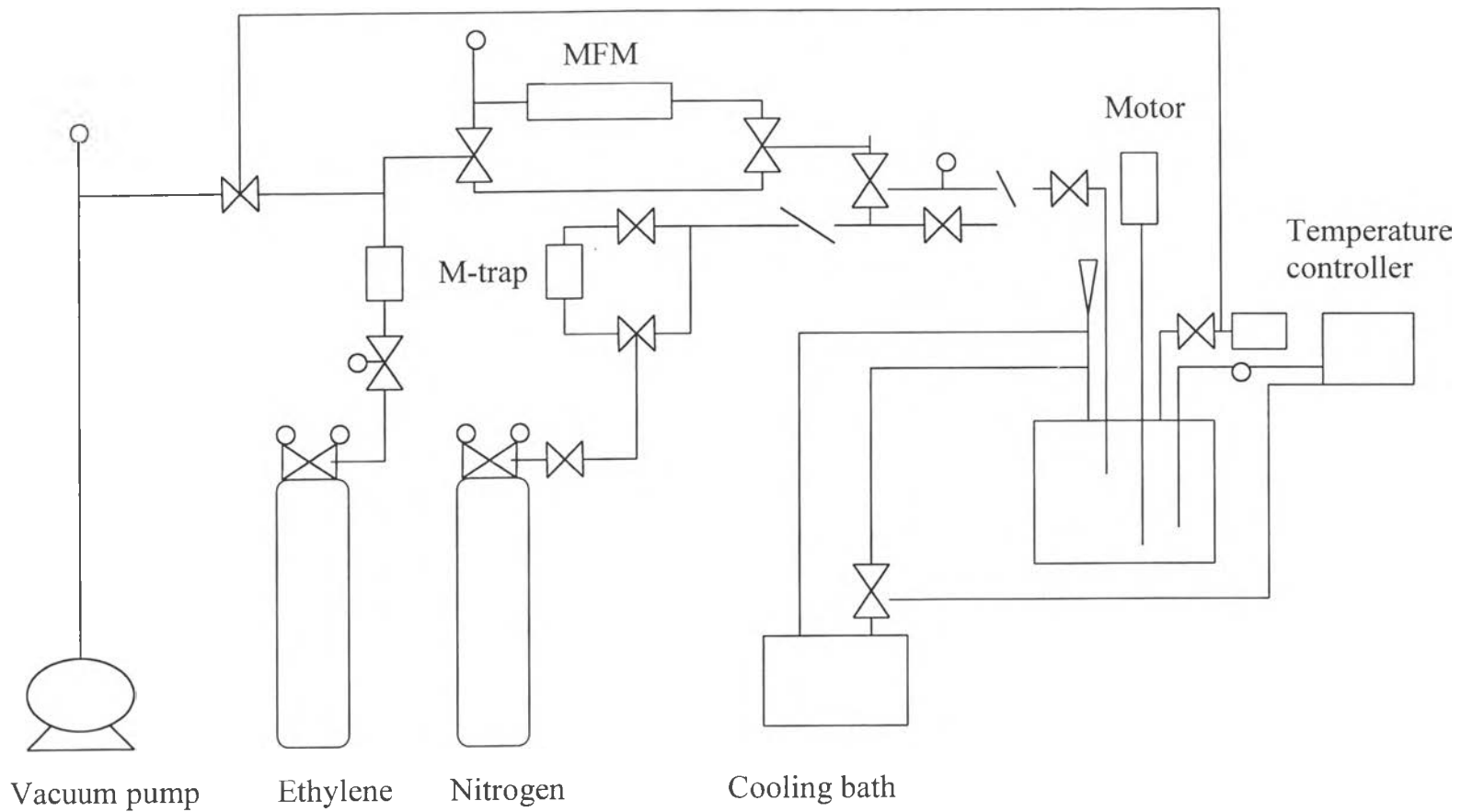


Figure 3.2 Schematic of experimental polymerization setup.

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 high-temperature GPC instrument equipped with three Waters Ultrastyrigel columns in series at 140°C. The columns have exclusion limits for polystyrene 10⁴, 10⁵ and 10⁶ Å pore size. The solvent, *o*-dichlorobenzene, was applied at a flow rate of 1.0 cm³/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 and its melting point were determined using a Perkin-Elmer DSC calorimeter. Each sample was heated from 50°C to 180°C with the heating rate of 20°C/min and was then cooled down to 50°C and again reheated at the same rate. The crystallinity was calculated from equation 3.1 below :

$$\%X = (\Delta H_f / \Delta H_f^*) \times 100 \quad (3.2)$$

The endothermic heat of fusion peak, ΔH_f , was obtained from the DSC thermogram (Figure 3.3). The heat of fusion of perfectly crystalline polyethylene, ΔH_f^* , was taken as 286 J/g (Gray, 1970).

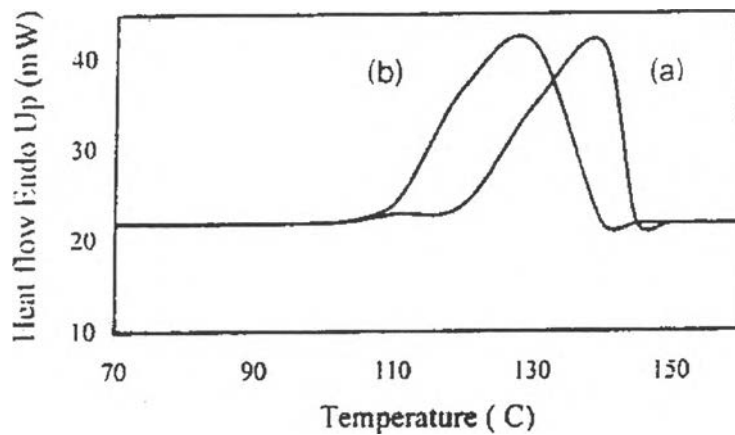


Figure 3.3 The DSC thermograms of the (a) first and (b) second scans of metallocene polyethylene.

3.3.3.3 Wide Angle X-ray Diffraction (WAXD)

Crystallinity was also obtained from WAXD (D/MAX-2000 series of Rigaku/X-ray Diffractometer system). The experiment was performed in the range 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 3.3 below

$$X = \frac{(A_1 + A_2)}{(A_1 + A_2 + A_3)} \quad (3.3)$$

Where $A_1 + A_2$ is the crystallinity peak area and $A_1 + A_2 + A_3$ is the total area under the curve. These values were obtained from the polyethylene X-ray diffraction pattern (Figure 3.4), where the sharp peak represents the crystalline areas and the broad peak represents the amorphous area.

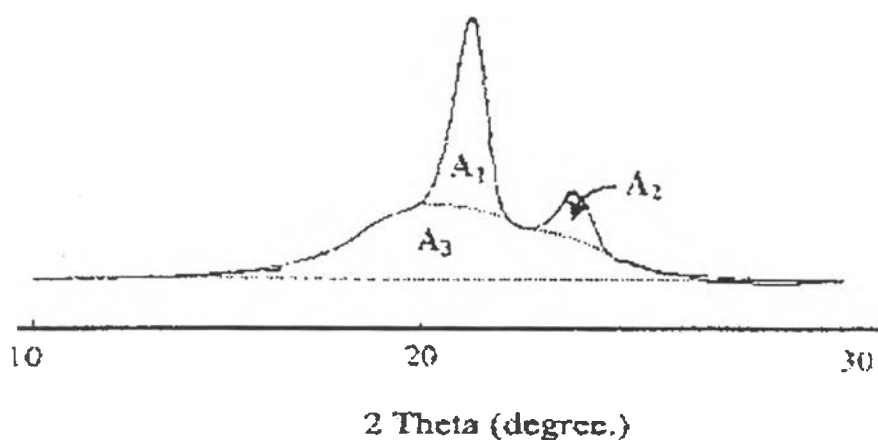


Figure 3.4 X-ray diffraction pattern.

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.

3.3.3.5 Fourier Transform Infrared Spectroscopy (FT-IR)

Polyethylene powder was dissolved in toluene at 140°C, spread on a petri dish, and heated in an oven at 80-90°C until dry. The spectra of the PE films were determined in the wavenumber range between 4000 and 400 cm^{-1} .