

CHAPTER IV

METHODOLOGY

4.1 Polymerization

4.1.1 Apparatus

The polymerization system consist of aparatus as following;

- A 2-litre stainless steel pressure reactor, Parr model 4842, equipped with variable speed motor and anchor-type agitator.
- Temperature Controller of MarkIV Company , model 2004.
- Balance of Oertling, model SC161. Weight capacity 16 kgs and sensitivity 0.1 g.
- Controlled Atmosphere Glove Box of Labconco, model 50800-02.

The apparatus is shown in figure 4.1

4.1.2 Raw materials

- Propylene* : The gas was supplied by
Thai Polyethylene Co.,Ltd.
- Toluene* : HPLC Grade from Baker Analyzed
(purged with UHP nitrogen before used)
- Methylaluminoxane* : 30% in toluene from Albemarle
Corporation

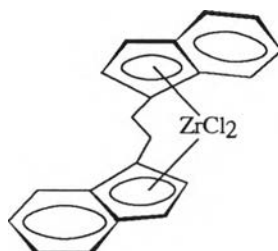
Properties

- Chemical Formula : (CH₃AlO)
- Extremely Flammable
- Reacts violently with water and air

rac-Eth(Ind)₂ZrCl₂ : Racemic-Ethylenebis(Indenyl)zirconium dichloride

Properties

- Chemical Formular : C₂H₄(C₉H₆)₂ZrCl₂
- Air and moisture sensitive
- Light sensitive



Nitrogen : Ultra High Purity (UHP) 99.999% supplied
by Thai Industrial Gas

Methanol : AR Grade from Baker Analyzed

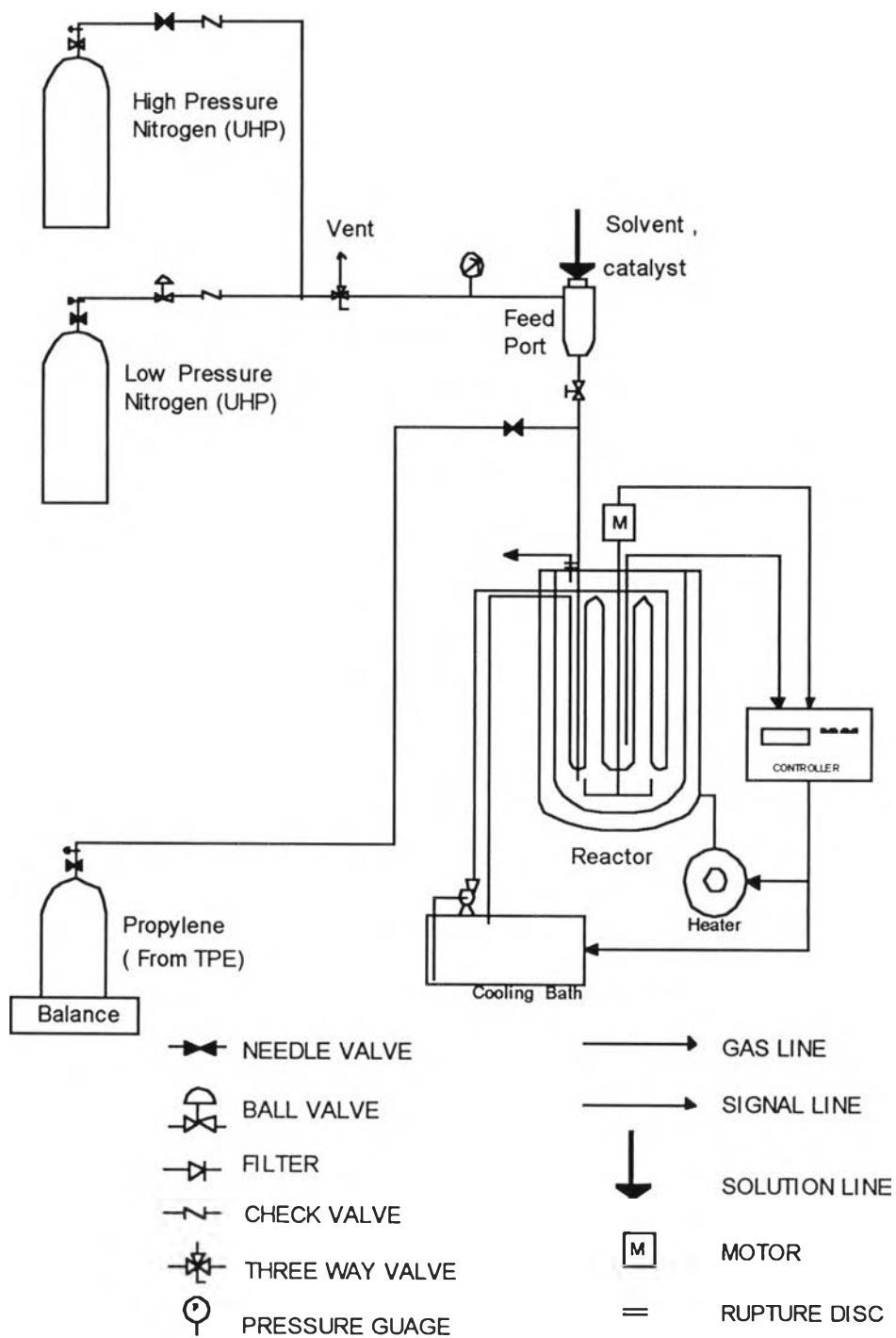


Figure 4.1 Schematic diagram of polymerization reactor.

4.1.3 Polymerization procedure

After the 2-litre reactor was set up, pressure testing was done at 30 bar above local atmospheric pressure for 1 hour. The pressure lost was less than 0.2 bar which was acceptable.

The reactor was purged with low pressure nitrogen (about 0.2-0.3 bar) for 1 hour at the polymerization temperature. The system was cooled down to room temperature for feeding propylene gas. The propylene gas tank was warmed up to 40°C for 5 mins. Reactor system was then purged with propylene at 0.5 bar three times in 15 mins. Finally, 200 grams of propylene gas was fed to the reactor.

After propylene was loaded, the reactor was brought to the polymerization temperature. During the process of heating up and cooling down, co-catalyst or methylaluminoxane (MAO) and toluene 100 ml were fed to the reactor by using the technique shown in figure 4.2. At the reactor temperature of 5°C lower than the desired operating temperature, catalyst or $\text{rac-Et(Ind)}_2\text{ZrCl}_2$ was fed to the reactor via the feed port and the timer was started. After feeding catalyst, toluene 100 ml was used to rinse the catalyst and the co-catalyst from the feed port into reactor. Due to the exothermic nature of the reaction, polymerization rate had to be controlled by cooling water. The reaction was carried on for 1 hour at the desired conditions.

A small amount of methanol was used to terminate the reaction after one hour. Then, the reactor was cooled down to room temperature and disconnected.

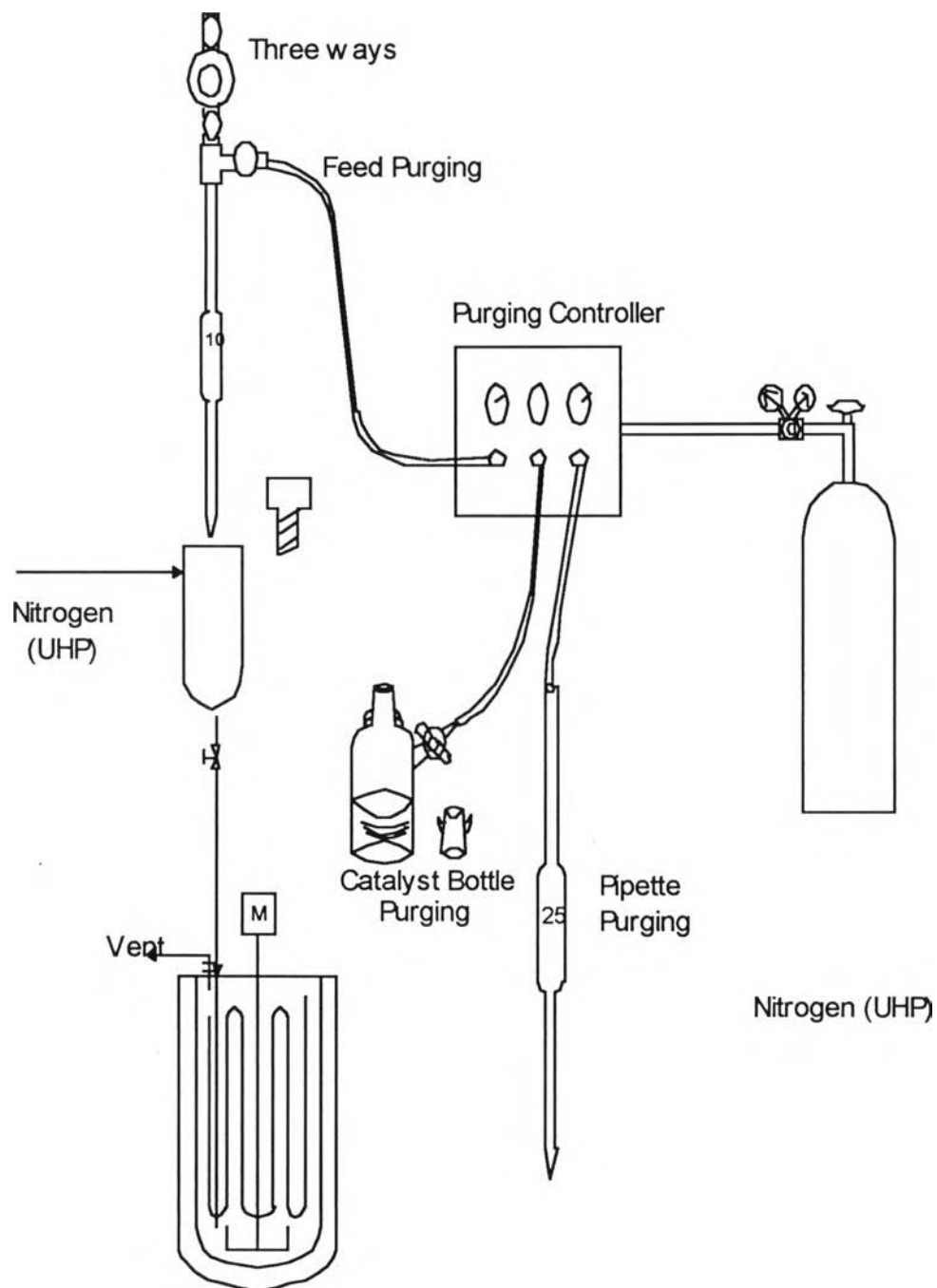


Figure 4.2 Schematic diagram of purging system.

The powder slurry inside the reactor was removed and dried in an oven at 80°C for 1 hour under a nitrogen atmosphere. The reactor was cleaned and assembled for next batch.

The weak point of this polymerization system was the feeding gas into system without oxygen trap. The catalyst, co-catalyst and solvent may be contaminated by oxygen.

Polypropylene was produced using the following compositions and reaction conditions.

- Temperature at -20, -10, 10, 20, 30, 40 and 50 °C
- Zirconium concentration at 1, 2, 5, 10, 20 and 25 μmole
- Aluminium to Zirconium ratio at 1,000; 2,000; 4,000; 5,000; 6,000; 8,000; and 10,000
- Weight of propylene at 100, 150, 200, 250 and 300 grams

Polypropylene samples from all conditions were characterized.

4.2 Characterization

The following characterization techniques were used:

- Fourier Transform Infrared Spectroscopy (FT-IR).
- Differential Scanning Calorimetry (DSC).
- Gel Permeation Chromatography (GPC).
- X-ray Diffraction Spectroscopy (XRD)

4.2.1 Chemicals

2 Dichlorobenzene : AR grade for polypropylene film preparation for FT-IR, was used as solvent for GPC analysis.

Liquid Nitrogen : Coolant in DSC.

n-hexane : Commercial grade was used as a releasing agent.

4.2.2 Procedure for characterization

4.2.2.1 Fourier transform infrared spectroscopy

2 Dichlorobenzene was used as a solvent for preparing PP films by the solvent casting method. 0.5% by weight of polypropylene was dissolved at 150°C. The solutions were spread on the surface of watch glasses and then heated in a conventional oven at 90-95°C for 1/2-1 hour. Polypropylene films were then released by dipping in n-hexane for 1/2 hour and, finally, transferred to an oven again to evaporate the n-hexane at 60°C.

The spectrum of PP films were measured by IR absorption with a BIO-RAD Digilab FTIR. The wavenumber range was between 4000 and 400 cm^{-1} . All of the IR spectra were measured with 8 cm^{-1} resolution and 16 number of scans. The ratio of absorbances at 995 and 970 cm^{-1} was used to estimate isotacticity by employing the calibration curve of Loungo (Figure 3.3).

4.2.2.2 Thermal analysis

The thermal behaviors of the PP samples were determined with a DuPont 910 S DSC. Samples of 5-7 mg were sealed in clamped aluminum sample pans. The temperature was programmed at 10°C/min. in all cases. Liquid nitrogen cooling accessory was used as a coolant system. After loading the samples into the instrument chamber, the chamber was purged with dry nitrogen at flow rate of 25 and 65 ml/min. for heating up and cooling down, respectively. The temperature was between 80 and 160°C.

The melting point was determined from the thermograms.

4.2.2.3 X-ray diffraction

X-ray diffraction measurements were made with Rigaku Rotating anode powder diffractometer. Monochromatized copper K- α line was used as the X-ray source.

The X-ray diffraction approach was made use of the fact that a totally amorphous polymer will not give rise to a sharp diffraction pattern, the other crystalline or microcrystalline material would diffract X-ray at specific angles. On the other hand, amorphous materials simply scatter X-ray in all directions. Thus the percent crystallinity of samples could be estimated from X-ray diffraction intensities.

4.2.2.4 Gel permeation chromatography

The molecular weight and molecular weight distribution of polypropylene sample were determined by WATERS GPC-150C using a mixed polystyrene gel column (SHODEX 1.AT 806/S-2.AT 804/S-3.AT 803/S) and *o*-dichlorobenzene as solvent, under following conditions;

Injection Temperature 140°C

Oven Temperature 140°C

Detector Temperature 140°C

Flow rate 1.0 ml/min.