

## CHAPTER IV

### EXPERIMENT

The experimental procedures in this study were divided into seven parts as follows,

- (i) Chemicals and Equipments
- (ii) Ziegler Natta Catalyst preparation
- (iii) Ethylene polymerization and propylene polymerization and termination polymerization by adding hydroxyl groups.
- (iv) Block Copolymer of polyethylene and polypropylene via diisocyanate
- (v) Blending of polyethylene with polypropylene , adding synthesized compatibilizers
- (vi) Molding preparations
- (vii) Characterized polymers blends

The details of each part were described below.

#### 4.1 Equipments and Chemicals

##### 4.1.1 Chemicals

1. Propylene gas ( $C_3H_6$ ) and Ethylene gas ( $C_2H_4$ ) was donated from National Petrochemical Public Company Limited (NPC), used without further purification.
2. Argon gas (Ultra High Purity, 99.999%) was purchased from Thai Industrial Gas Co., Ltd. (TIG) and was purified by passing through the column packed with molecular sieve 3 Å, BASF Catalyst R3-11G, sodium

hydroxide (NaOH) and phosphorus pentoxide ( $P_2O_5$ ) to remove traces of oxygen and moisture.

3. Oxygen gas (UHP) was obtained from Thai Industrial Gas Co., Ltd.
4. Hexane ( $C_6H_{14}$ ) polymerization grade was received from Esso chemical (Thailand) Co., Ltd. It was dried over dehydrated  $CaCl_2$  and was distilled over sodium/benzophenone under argon atmosphere.
5. diisocyanato-diphenylmethane (MDI) were donated from Bangkok Polyethylene Co., Ltd., Thailand.
6. Titanium tetrachloride ( $TiCl_4$ , > 99%) was purchased from MERCK.
7. Triethylaluminum ( $Al(C_2H_5)_3$ ) ,diluted in hexane, was donated from Bangkok Polyethylene Co.,Ltd. (Thailand).
8. Anhydrous magnesium chloride ( $MgCl_2$ , >98%) was purchased from Sigma.
9. Diethylphthalate ( $C_{12}H_{14}O_4$ , 98%) was supplied from Fluka Chemical Industries.
10. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
11. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.
12. Methanol (Commercial grade) was purchased from SR lab.

#### **4.1.2 Equipments**

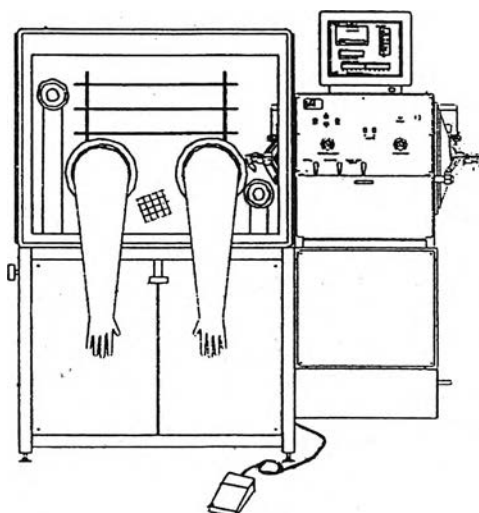
All types of equipments used in the catalyst preparation, polymerization and polymer blends are listed below:

##### **4.1.2.1 Synthesis Part**

###### **(a) Glove box**

Glove Box System 30905C manufactured by Vacuum Atmospheres Company, USA 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. The glove box is shown in Figure 4.2.1(a).



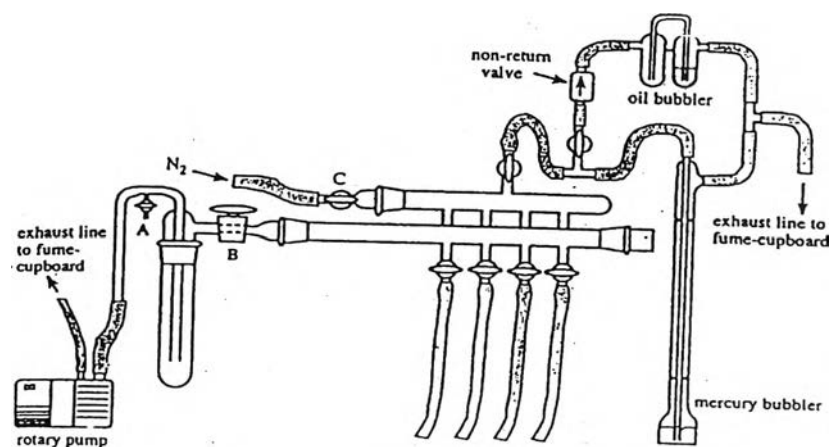
**Figure 4.1.1(a)** Glove box

**(b) Schlenk line**

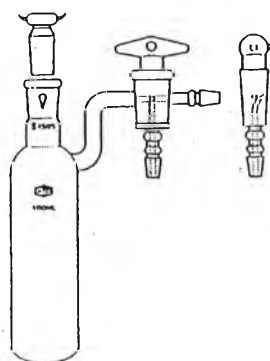
Schlenk line included of vacuum line connected to vacuum pump and argon line for purging when reagents are transferred. The schlenk line was shown in Figure 4.2.1(b).

**(c) Schlenk Tubes**

A schlenk tube is a tube with a glass ground joint and a side arm with three way glass valve. Size of the Schlenk tubes were 50, 100, and 200 m. They were used to synthesize catalyst precursor and collect "materials which were sensitive to oxygen and moisture.



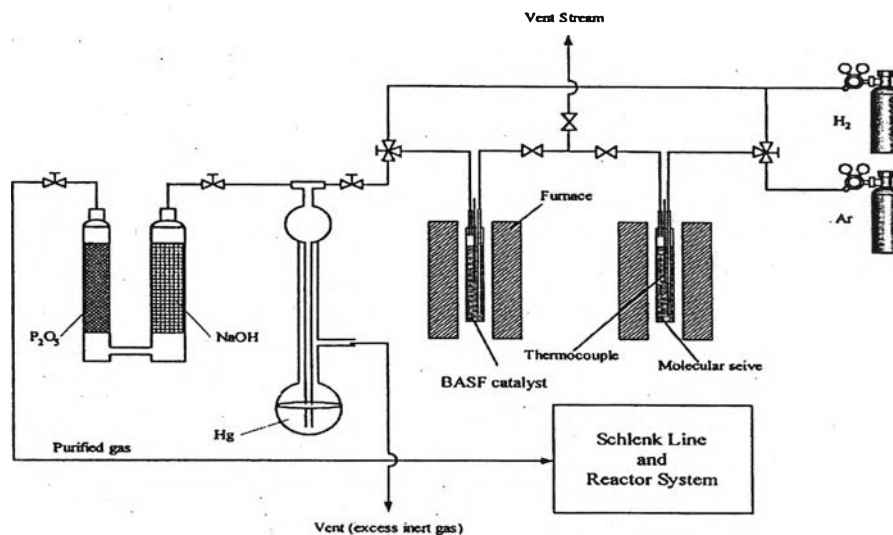
**Figure 4.1.2 (b) Schlenk line**



**Figure 4.1.3 (c) Schlenk tube**

**(d) The inert gas supply**

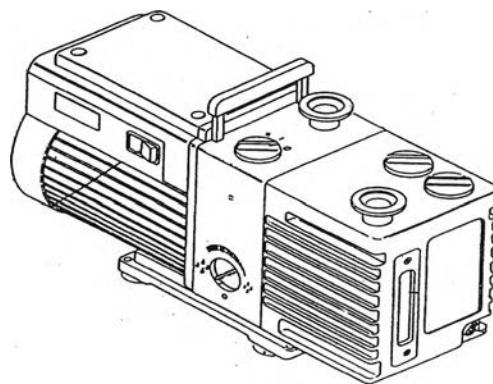
The inert gas (argon) was pass through columns of oxygen trap (BASF catalyst, R3-11G), moisture trap (molecular sieve), sodium hydroxide (NaOH) and phosphorus pentaoxide ( $P_2O_5$ ) for purifying ultra high purity argon before use in Schlenk line and solvent distillation column. The inert gas supply system is shown in Figure 4.1.2.3(d).



**Figure 4.1.4 (d) Inert gas supply system**

**(e) The vacuum pump**

The Vacuum pump model 195 from Labconco Corporation 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. The vacuum pump is shown in Figure 4.2.1(e).



**Figure 4.1.5 (e) Vacuum pump**

**(f) Reactor**

A 100 ml stainless steel autoclave was used as the polymerization reactor.

### **(g) Magnetic stirrer and Hot plate**

The magnetic stirrer and hot plate Model RCT Basic from IKA Labortechnik were used.

#### **4.2.2.2 Polymer Blend Part**

##### **(a) Digital hot plate stirrer**

A Cole-Parmer digital hot plate stirrer was used for mixing the polymers with additives. This hot plate stirrer is programmable. All functions can be set from digital panel and display their status on LCD. The plate temperature, stirrer speed and time are controllable.

##### **(b) Hydraulic hot press**

A local made hydraulic hot plate was used in these experiments. The maximum working temperature of this machine is 600 °c and the maximum pressure is 5,000 psi. This equipment was used for prepare the sample for rheology test.

## **4.2 Preparation of Ziegler-Natta Precursor**

0.476 g of Anhydrous magnesium chloride, 2.5 ml of decane and 2.34 ml of 2-ethylhexanol were reacted at 130 °C for 2 hours to form a uniform solution. Phthalic anhydride 0.109 g was added to solution, and the mixture was stirred at 130 °C for 1 hour to dissolve phthalic anhydride. The resulting, uniform solution was cooled to room temperature, and wholly drop wise over the course of 1 hour to 20 ml of titanium tetrachloride kept at -20 °C. After the addition, the mixture was heated to 110 °C over the course of 4 hours. When the temperature reached 110 °C, 0.26 ml of diethylphthalate was added. The mixture was maintained at this temperature for 2 hours. After the reaction for 2 hours, the solid portion was collected from the reaction mixture. The solid portion was again suspended in 20 ml of titanium tetrachloride and

again reacted at 120 °C for 2 hours. After the reaction, the solid portion was again collected then washed with 10 ml of decane and with 10 ml of hexane 3 times. The resulting solid was dried in vacuum.

#### 4.3 Polymerization of Polyethylene and Polypropylene terminal hydroxyl group Procedure

The propylene polymerization and ethylene polymerization reactions were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110 °C for 30 minutes before use. Solvent, catalyst and cocatalyst were introduced into the autoclave and stirred for 5 minutes at room temperature in the glove box. After that, the reactor was frozen in liquid nitrogen to stop reaction and then the autoclave was evacuated to remove the argon, and the reactor was placed in the water bath to control the temperature. The polymerization was started by feeding gas (propylene or ethylene). The polymerization was carried out for 90 minutes, and then stopped the polymerization by directly brought into contact with oxygen gas at room temperature followed by addition of hydrochloric acid solution in methanol and dried at room temperature.

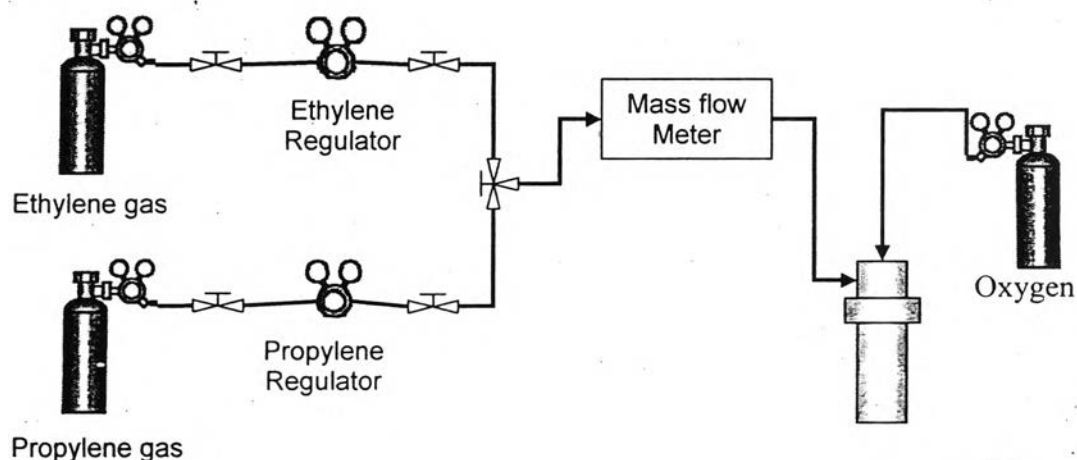
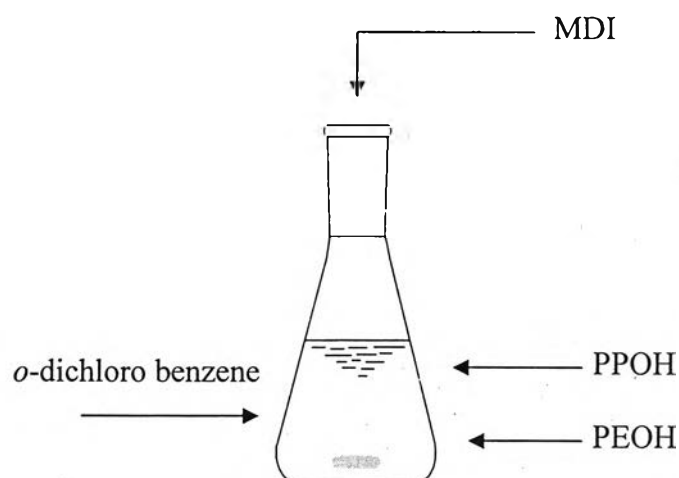


Figure 4.3 Polymerization line



#### 4.4 Blocking Copolymerization

Copolymerization was carried out in a glass reactor equipped with magnetic stirrer. Polyethylene and polypropylene containing hydroxyl group 50/50 %wt were added and dissolved in *o*-dichlorobenzene at 120 °C. Follow by dropped of excess MDI in the solution that remained stir for 1 hr. The solution was washed with excess methanol. Polymer was filtered and dried.



**Figure 4.4** Blocking copolymerization

#### 4.5 Blending Preparation

The blends were made by melt mixing at 230 °C by hand on the digital controllable hotplate with various compositions. All the samples were kept at 300°C for five minutes and immediately quenched to 200°C for twenty minutes before further experiments at room temperature.



## 4.6 Molding Preparation

After blending, all polymer blends was molded with Automatic Hydraulic Hot Press. Hot Press was opened to warm at 270 °C before using about half hours. Then steel plate that coated with aluminium foil, aluminium mould and blend polymer were putted down to Hot Press respectively. When the polymer blend was melt, other steel plate that coated with aluminium foil was putted down to melt blend polymer. Next they will be slowly compressed until 1500 psi. The blend polymer was annealed at 280°C by kept in Hot Press about 5 minutes. The size of blend polymer after molding was 10x50x0.5 mm for dynamic mechanical analysis and tensile testing.

## 4.7 Characterization Instruments

### 4.7.1 Scanning Electron Microscope (SEM)

All distribution on the polymer particles are investigated by Scanning Electron Microscope (SEM),JSM-640 Scanning Microscope,Microspec WDX at Technological Research Equipment Center,Chulalongkorn University,with Energy Dispersive X-ray analysis (EDX).

### 4.7.2 Gel Permeation Chromatography (GPC)

The method of determination of molecular weight (Mw) and molecular weight distribution (MWD) was gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography (SEC) to separate samples of polydispersed polymers into fractions of narrower molecular weight distribution. In this using GPC Model: Waters 2000 Column: Styragel HT6E with 1,2,4-Trichlorobenzene as a solvent at 135 °C.

### 4.7.3 Infrared Spectroscopy (FTIR)

Infrared survey spectra were recorded with FTIR (IFS28) The scanning ranged from 400 to 4000  $\text{cm}^{-1}$  on the pallet sample of KBr powder with scanning 12 times.

### 4.7.4 $^{13}\text{C}$ -Nuclear Magnetic Resonance ( $^{13}\text{C}$ -NMR)

$^{13}\text{C}$ -NMR spectroscopy was 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.

### 4.7.5 Differential Scanning Calorimetry (DSC)

The glass transition temperature ( $T_g$ ), crystalline temperature ( $T_c$ ) and crystalline melting point temperature ( $T_m$ ) of polymer were determined by a Perkin-Elmer Diamond DSC over the range -60 to 200  $^{\circ}\text{C}$  of scanning rate 40  $^{\circ}\text{C}/\text{min}$  under nitrogen atmosphere. The heating cycle was run twice. The first scan, samples were heated and then cooled to room temperature. In the second scan, samples were reheated at the same rate. The results of the second scan were represented the crystallization from cooling at the same rate. The first scan was influenced by the mechanical and thermal history of samples.



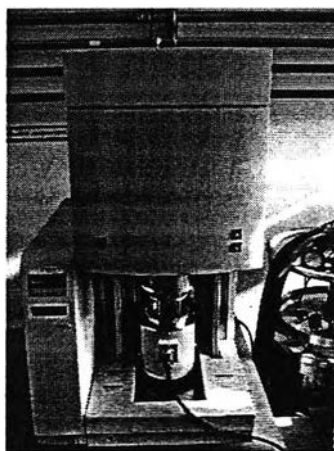
**Figure 4.7.1** Differential Scanning Calorimetry (DSC) Equipment

#### 4.7.6 Dynamic Mechanical Analysis (DMA)

Dynamic mechanical properties of blending polymers were determined by using Dynamic Mechanical Analysis (DMA) with a Perkin-Elmer DMA-Pyris Diamond. The samples after molding were cut for standard DMA samples (10x25x0.5 mm). Condition and parameters were shown in Table below.

**Table 4.7.1** Conditions and parameter for running DMA

Conditions and parameter	Value
Sample size(w x l x t) (mm)	10 x 20x0.5
DMS Measurement Mode	Tension
Temperature Control Mode	Ramp (1.5 °C/min)
DMS frequency (Hz)	0.1, 0.2, 0.5, 1.0, 2.0, 5.0, 10.0
Temperature range	-130 to 150 °C
L Amplitude (µm)	10
Minimum Tension/Compression Force(mN)	200
Tension/Compression Force gain	1.5
Force Amplitude Default Value (mN)	4000
Nitrogen as carrier gas (ml/min)	100



**Figure 4.7.2** Dynamic Mechanical Analysis (DMA) Equipment

#### 4.7.7 Tensile testing machine

Tensile properties were characterized using an Instron universal testing machine with a test speed of 12.5 mm/min. The tests were conducted according ASTM D 882-02.

The tensile testing machine of a constant-rate-of-crosshead movement is used. It has a fixed or essentially stationary member carrying one grip, and a moveable member carrying a second grip. Self-aligning grips employed for holding the test specimen between the fixed member and moveable member prevent alignment problems. An extension indicator is used to determine the distance between two designated points located within the gauge length of the test specimen as the specimen is stretched.

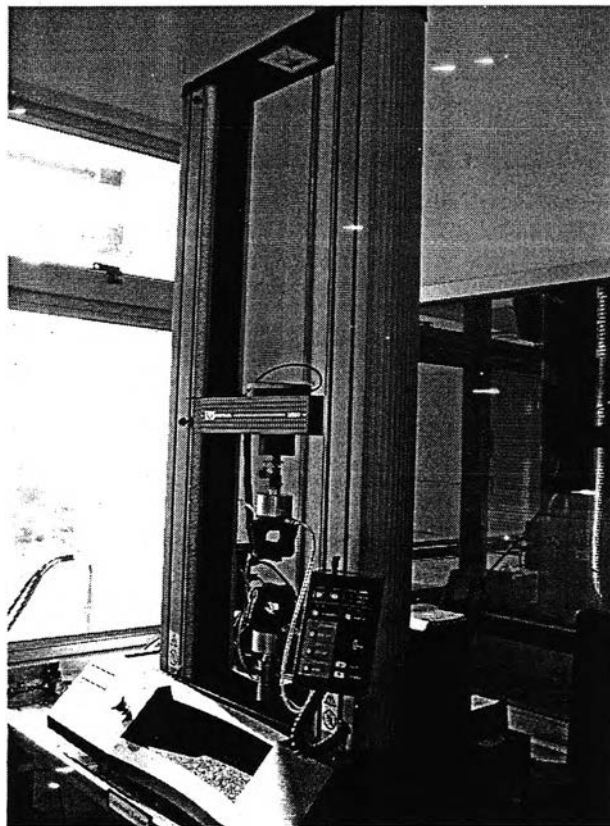
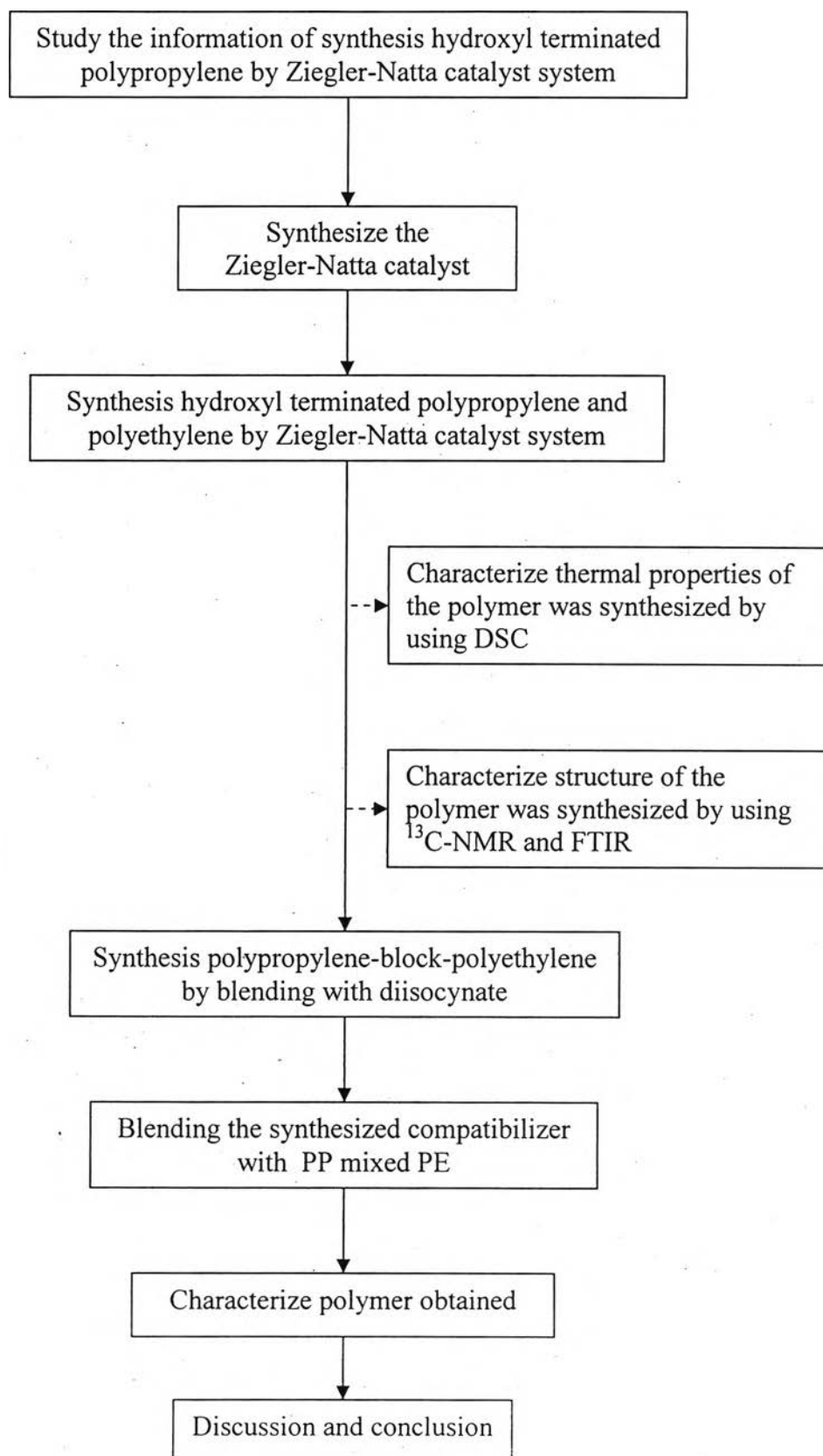


Figure 4.7.3 Universal Testing Machine equipment



**Figure 4.8** Flow diagram of research methodology