

CHAPTER IV

EXPERIMENT

In this chapter, the materials and chemicals, equipments, catalyst preparation, polymerization procedure, characterization instruments and sample preparations will be explained.

4.1 Materials and Chemical

The chemicals used in these experiments were analytical grade, but only critical materials were specified as followed:

1. Ethylene (C_2H_4) and Propylene (C_3H_6) gas were 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. Hexane (C_6H_{14}) was received from Esso chemical (Thailand) Co., Ltd. It was dried over dehydrated $CaCl_2$ and was distilled over sodium/benzophenone under argon atmosphere.
4. Titanium tetrachloride ($TiCl_4$, > 99%) was purchased from MERCK.
5. Triethylaluminum ($Al(C_2H_5)_3$) ,diluted in hexane, was donated from Bangkok Polyethylene Co.,Ltd. (Thailand).
6. Anhydrous magnesium chloride ($MgCl_2$, >98%) was purchased from Sigma.
7. Diethylphthalate ($C_{12}H_{14}O_4$, 98%) was supplied from Fluka Chemical Industries.

8. 2-Ethylhexanol ($C_8H_{18}O$, >99%) was received from Fluka Chemical Industries.
9. Phthalicanhydride ($C_8H_4O_3$, >97) was received from Fluka Chemical Industries.
10. Decane ($C_{10}H_{22}$, >98%) was supplied from Fluka Chemical Industries.
11. Benzophenone (purum 99.0%) was obtained from Fluka Chemie A.G. Switzerland.
12. Calcium chloride (Dehydrated) was manufactured from Fluka Chemie A.G. Switzerland.
13. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.
14. Methanol (Commercial grade) was purchased from SR lab.
15. Sodium (lump in kerosene, 99.0%) was supplied from Alrich chemical Company, Inc.
16. 1100RC Polypropylene resin was purchased from Thai Petrochemical Industry Public Co.,Ltd.

4.2 Equipments

All equipments used in the catalyst preparation, preparation and polymerization of the polymer, blending of polymer, and polymer characterization are listed as below:

4.2.1 Glove Box

Glove Box System 30905C manufactured Vacuum Atmospheres Company, USA. It includes 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 4.1.

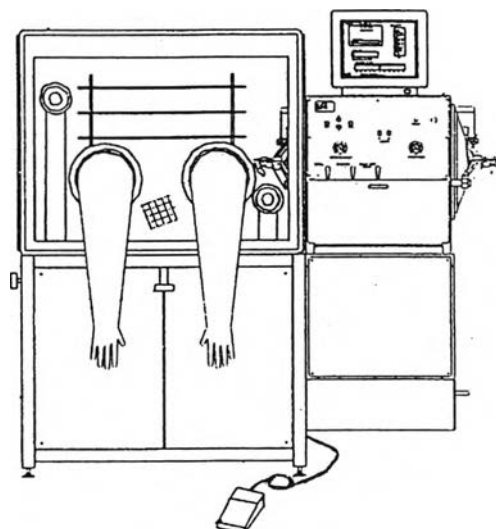


Figure 4.1 Glove box

4.2.2 Schlenk Line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contains enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in Figure 4.2.

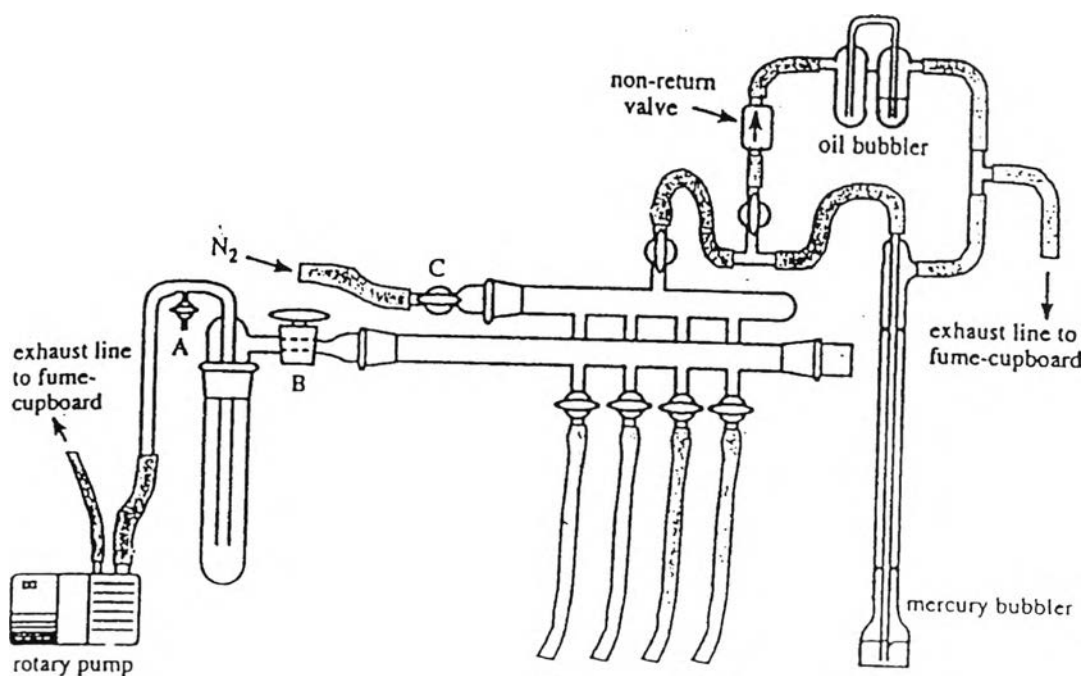


Figure 4.2 Schlenk line

4.2.3 Schlenk Tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 4.3. Sizes of Schlenk tubes were 50 and 100 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture under argon atmosphere outside the glove box. It was used accompanied with the Schlenk line.

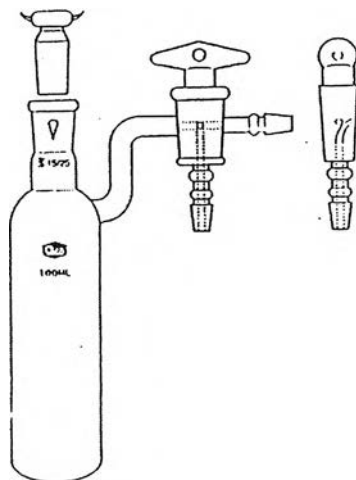


Figure 4.3 Schlenk tube

4.2.4 Cooling System

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

4.2.5 Inert Gas Supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3A to remove moisture, sodium hydroxide (NaOH) and phosphorus pentoxide (P_2O_5) for purifying ultra high purity argon before use in Schlenk line and solvent distillation column. The oxygen scavenger was regenerated by treatment with hydrogen at 300 °C for 2 hours before flowing the argon gas through all of the above columns. The inert gas supply system is shown in Figure 4.4.

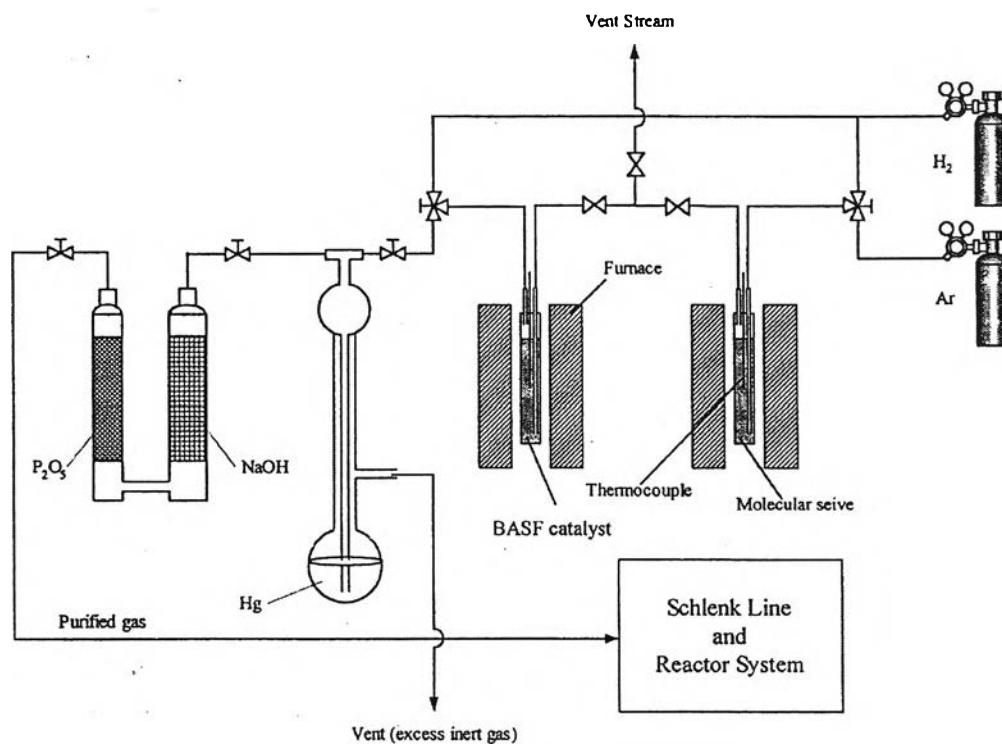


Figure 4.4 Inert gas supply system

4.2.6 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 4.5.

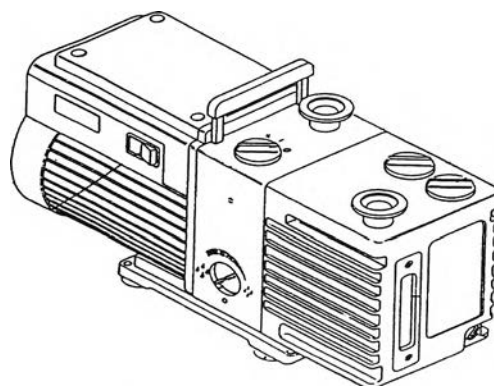


Figure 4.5 Vacuum pump

4.2.7 Reactor

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

4.2.8 Polymerization Line

The polymerization line consists of ethylene gas, propylene gas, pressure regulator, and valve system. This line used for polymer synthesis, control pressure and type of gas for polymerization. The polymerization line is shown in Figure 4.6.

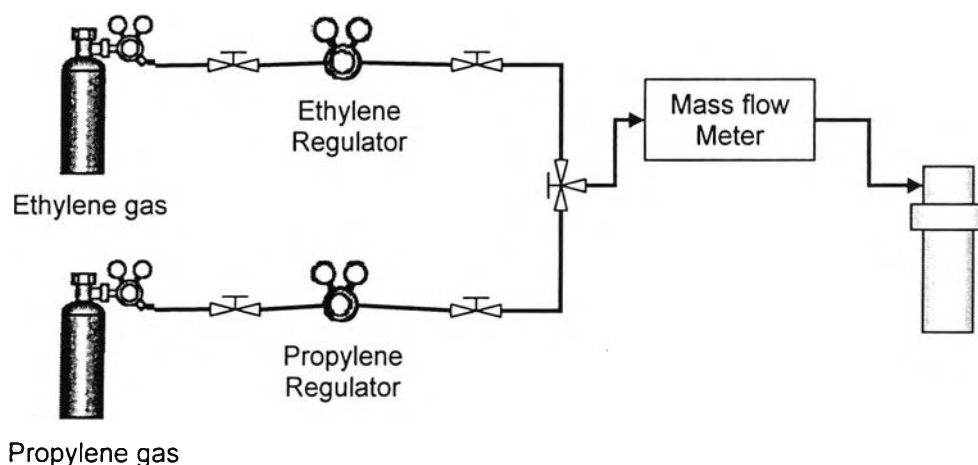


Figure 4.6 Polymerization line

4.2.9 Magnetic Stirrer and Hot Plate

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

4.2.10 Aluminium moulds

Aluminium moulds 100×100×0.5 mm. with drilled 10×50×0.5 mm and 2 Steel plates 150×150×2 mm were purchased from P. Konlakan Machinery Tool.

4.2.11 Syringe, Needle and Septum

The syringes were used in the experiment had a volume of 50 and 10 ml and the needle were No. 17 and 20, respectively. The septum was a silicone rod. It was used to prevent the surrounding air from entering into glass bottle by blocking at the needle end. The solvent, catalyst, cocatalyst and monomer were transferred to a glass reactor by using needles.

4.2.12 Digital Hot Plate Stirrer

A Cole-Parmer digital hot plate stirrer was used for blending the polymers. The 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.

4.2.13 Automatic Hydraulic Hot Press

The LAB TECH hydraulic hot press LP-50 M/C 9701 was used for preparing the thin film form polymer blend. It has both the automatic mode and manual mode. In automatic mode, it has four steps (preheat, vent, full press and cooling step), that can be controlled in one touch which times adjustment of each of step separately. The hot press can be compressed up to maximum 50 ton (160 kg/cm^2).

4.2.14 Surface Temperature Probe and Digital Thermometer

The Cole-Palmer surface probe model E-08516-60 with 0.5 inch tip diameter, which has a temperature range from -250 to $649 \text{ }^\circ\text{C}$, was used for measuring the temperature during the mixing of sample and measuring the temperature of hot plate during the phase separation of miscible samples.

4.3 Procedures

All operations were performed under argon atmosphere by using Schlenk line and glove box.

4.3.1 Ziegler-Natta catalyst preparation procedure

Anhydrous magnesium chloride (MgCl_2) (0.476 g), 2.5 ml of decane and 2.34 ml of 2-ethylhexanol were added into a schlenk tube and heated to $130 \text{ }^\circ\text{C}$ for 2 h under magnetic stirring and argon atmosphere. Then phthalic anhydride was introduced 0.109 g into the solution and stirred until MgCl_2 was completely dissolved. The resulting, uniform solution was cooled to room temperature, and wholly dropped wise over the course of 1 hour to 20 ml of titanium tetrachloride (TiCl_4) kept at $-20 \text{ }^\circ\text{C}$

under stirring. After the addition, the mixture was heated to 110 °C over the course of 4 hours. The temperature was then raised to 80 °C, and 0.26 ml of diethylphthalate was injected in. 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 these, 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 subjected to vacuum dry to form a powder in gray color which needed to be stored under argon.

4.3.2 Propylene polymerization procedure

The propylene 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.

Hexane as solvent, catalyst (catalyst concentration = 2.1×10^{-4} M) and Triethylaluminum (TEA) as cocatalyst ($Al_{(TEA)}/Ti$ ratio = 167) were introduced into the autoclave (total volume = 30 ml) 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 propylene gas (30 psi) and then stopped the polymerization by venting propylene gas and adding acidified methanol (HCl/methanol solution). The precipitated polymer was washed with excess methanol and dried at room temperature.

4.3.3 Synthesis of polypropylene-co-poly(ethylene-co-propylene)

Copolymerization was carried out in 100 ml stainless steel autoclave reactor with magnetic stirrer in hexane (total volume = 30 ml) by using $TiCl_4/MgCl_2/DEP-TEA$ catalytic system (catalyst concentration = 2.1×10^{-4} M and $Al_{(TEA)}/Ti$ ratio = 167). The polymer was synthesized in a two-stage reaction process. First, catalyst, cocatalyst and solvent were added into the reactor. The reactor was immediately put

into liquid nitrogen to stop the reaction between the catalyst and cocatalyst. After that, the reactor was evacuated to remove argon. Then, the reactor was taken out of liquid nitrogen and heated up to polymerization temperature. The first stage of polymerization concerned with propylene homopolymerization by fed only propylene gas into the reactor (10 minute). The reactor was heated under the controlled temperature to start the polymerization reaction. The second stage to cooperate the ethylene in the PP structure was successively done by suddenly feeding the pure ethylene gas to a stirred reactor (30 minute). The mixture was quenched by addition of HCl/methanol solution after completion of the reactions. The obtained polymer that precipitated out was washed with excess methanol and dried at room temperature.

4.3.4 Blending Preparation

The blends were made by melt mixing at 200°C by hand on the digital controllable hot plate with various percentages of polymers. The blends were followed by melt polypropylene and polypropylene-*co*-poly(ethylene-propylene) copolymer and gradually mixed by spoon on digital hotplate until both polymers was mixed completely (20 minutes approximately).

4.3.5 Molding Preparation

Blended polymer was molded with Automatic Hydraulic Hot Press. Hot Press was opened to warm at 190 °C before using. 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 (10 minutes approximately), other steel plate that coated with aluminium foil was putted down to melt blend polymer and slowly compressed until 1500 psi. The blend polymer was annealed at 190 °C by kept in Hot Press about 5 minutes.

4.4 Characterization

The instruments used to characterize all polymer products (pure and blend polymers) and operated conditions were specified in the following:

4.4.1 Thermal properties

The melting temperature (T_m) crystalline temperature (T_c) and glass transition temperature (T_g) of the polymer was determined with differential scanning calorimetry (DSC) which an instrument designed to measure the thermal properties. The melting temperature of polymers was determined from the critical point of DSC curve.

Perkin-Elmer Diamond DSC at Center of excellent on Catalytic and Catalytic reaction Engineering, Chulalongkorn University, was used in this research. The analyses were performed at heating rate 40 °C/min in the temperature range -60 to 200 °C. The heating cycle was run twice. The first scan, samples were heated and then cooled to start temperature. The second scan, samples were reheated at the same rate, but only the results of the second scan were reported because the first scan were influenced by the mechanical and thermal history of samples.



Figure 4.7 Perkin-Elmer Diamond DSC

4.4.2 Molecular Weight and Molecular Weight Distribution

One of the most widely used methods for the routine determination of molecular weight (M_w) and molecular weight distribution (MWD) was gel permeation chromatography (GPC) to separate samples of polydispersed polymers into fractions of narrower molecular weight distribution. The polymer products were dissolved in trichlorobenzene and operated at 135 °C

The molecular weight and molecular weight distribution were determined using gel permeation chromatography (GPC, Waters 2000) with Styragel HT6E column at 135 °C by 1,2,4-Trichlorobenzene as a solvent.

4.4.3 Co-monomer incorporation and Polymer structure

Nuclear magnetic resonance (NMR) spectroscopy is one of the most powerful tools available to the chemists and biochemist for elucidating the structure of both organic and inorganic species. For polymer, ^{13}C -NMR spectroscopy was widely used methods for determination of comonomer incorporation and polymer structure.

Sample solution were prepared in *o*-dichlorobenzene and benzene- d_6 (~20 vol%) for internal lock signal. ^{13}C NMR spectra were records on JEOL JNM-A500 Nuclear Magnetic Resonance Spectrometer at Chemical department, Faculty of science, Chulalongkorn University.

4.4.4 Morphology

Scanning electron microscopic (SEM) technique was the effective method to investigate catalyst precursor morphologies. The term of morphology was referred to shape, texture or form of polymer, and all distribution on the polymer particles.

JSM-640 Scanning Microscope, Microspec WDX at Technological Research Equipment Center, Chulalongkorn University, with Energy Dispersive X-ray analysis (EDX) was used in this research.

The samples for SEM analysis were coated with gold particles by ion sputtering device provide electrical contact to the specimens.



4.4.5 Dynamic mechanical properties.

Dynamic mechanical analysis (DMA) was performed to determine E' , E'' and $\tan\delta$ curve as the function of frequency and time.

Dynamic mechanical properties of blending polymers were characterized using Perkin-Elmer DMA-Pyris Diamond. All the experiments were operated at 0.1, 0.2, 0.5, 1, 2, 5, and 10 Hz in tension mode over the temperature range -140 to 150 °C with 1.5 °C/min and sample size were 10×50×0.5 mm, using liquid nitrogen as a cryogenic medium.

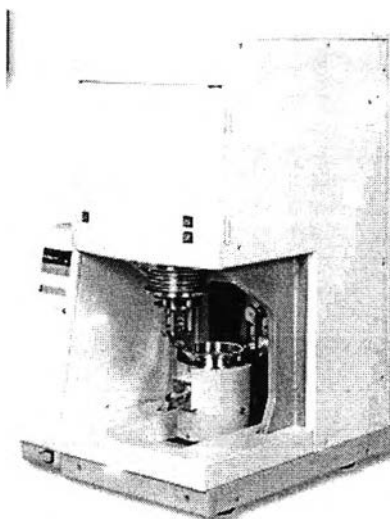


Figure 4.8 Perkin-Elmer Diamond DMA

4.4.6 Tensile strength

Tensile testing machine was used to characterize tensile strength of material. Obtained results are the stress-strain behaviors of material.

In polymeric material, tensile testing machine was determined mechanical properties of polymeric material such as tensile stress, tensile strain, modulus and toughness etc. The average tensile value of 5 specimens was used. In this study, the cross head speed was set constant rate of 12.5 mm/min and 10 kN of load cell. Tensile testing machine at Center of excellent on Catalytic and Catalytic reaction Engineering, Chulalongkorn University, was used in this research.

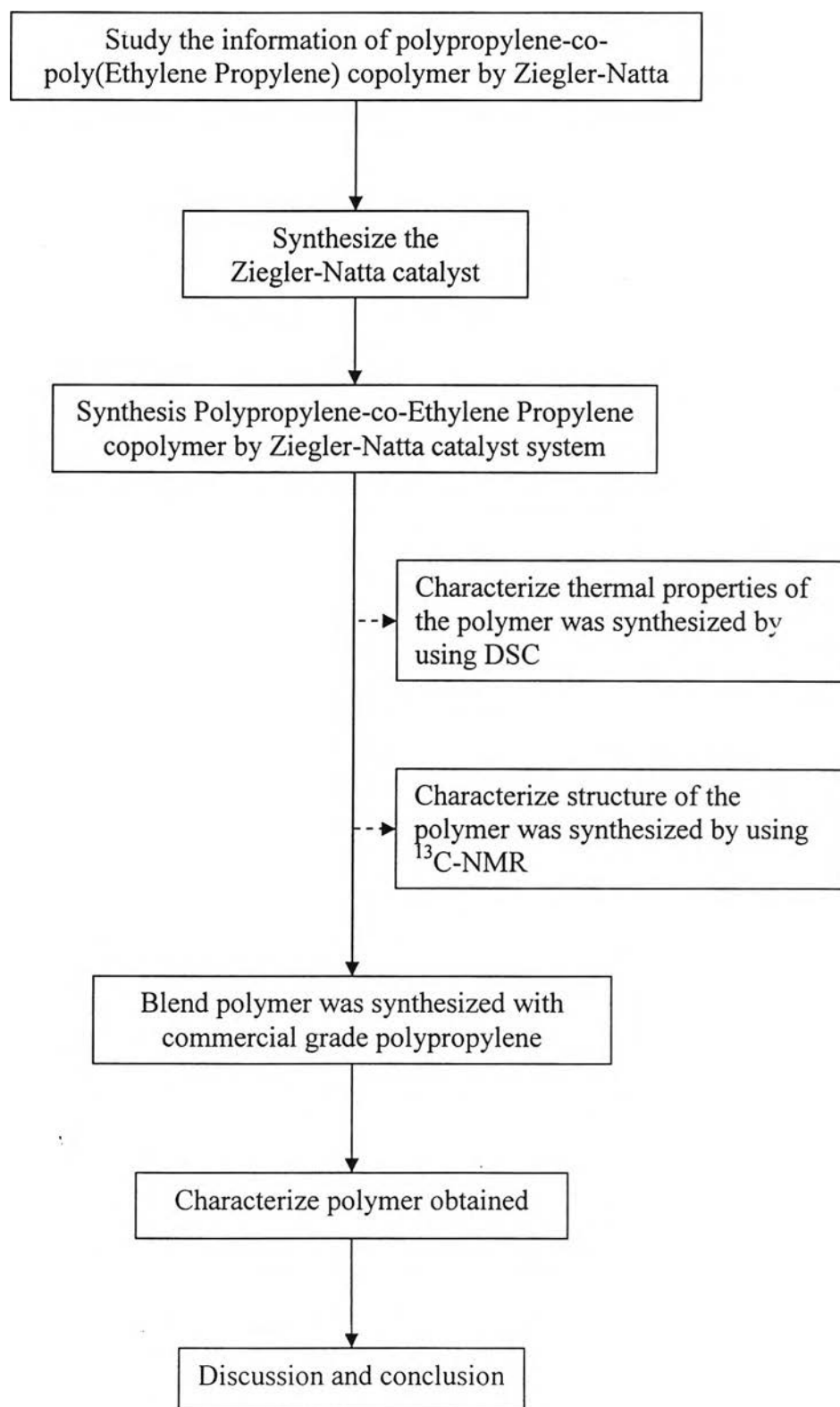


Figure 4.9 Flow diagram of research methodology