CHAPTER III
EXPERIMENTAL

These experimental studies of the polymerizations of propylene on Ziegler-Natta catalyst with and without external donor were performed at 70°C for 1 hour. In addition, effect of external donor/cocatalyst, cocatalyst/catalyst and hydrogen content were investigated on activity, isotactic index, melting temperature and crystallization temperature. Moreover, molecular weights (MW) and molecular weight distributions (MWD) were also characterized from polypropylene resins.

3.1 Materials

3.1.1 Gases

Propylene (polymerization grade) supplied by Thai Olefin Co., Ltd. was dried over molecular sieves (3°A).

Hydrogen (ultra high purity grade) supplied by Thai Industrial Gas Co., Ltd. was used as received.

Nitrogen (ultra high purity grade) supplied by Thai Industrial Gas Co., Ltd. was used as received.

3.1.2 Catalysts

$MgCl_2$-Supported titanium halide with dibutylphthalate catalyst was used.

Triethylaluminium supplied by Nippon Alkyls Company was used as received.

Dicyclopentyldimethoxysilane was used as external donor.

Diisopropyldimethoxysilane was used as external donor.

Isobutylisopropyldimethoxysilane was used as external donor.

Diisobutyldimethoxysilane was used as external donor

Cyclohexylmethyldimethoxysilane was used as external donor.

3.1.3 Chemicals

n-Hexane (commercial grade) supplied by Shell Chemicals (Public) Co. was used after fractional distillation.

Ethanol supplied by Merck Co., Ltd. was used as received.

3.2 Apparatus

1. A 2-litre jacketed stainless steel autoclave equipped with a variable speed motor, an anchor-type agitator, and temperature control unit.
2. Philips 8700 spectrophotometer, for measuring total titanium content of catalyst.
3. Melt flow index tester of KAYENESS, model 4000, for measuring the melt flow index of propylene polymer.
4. Gel Permeation Chromatography (GPC) of Waters, model 150-C, for measuring the molecular weight of propylene polymer.
5. A Soxhlet-type extractor with a boiling solvent, for measuring isotactic index of propylene polymer.
6. Differential Scanning Calorimeter (DSC) of Perkin-Elmer, model DSC-7, for measuring the melting temperature and crystalline temperature of propylene polymer.

3.3 Analysis of Total Titanium Content

The total Ti in the catalyst and the complexes of $TiCl_4$ was determined using the colorimetric method (Vogel, 1950). A known amount of catalyst was

dissolved to 10 ml of concentrated sulfuric acid and 10 ml of 3% H_2O_2. The solution was diluted to 100 ml with distilled water. The UV-VIS absorbance of the solution at 410 nm was measured with a Philips 8700 spectrophotometer. The wt % of Ti was then calculated from a calibration curve derived from the absorbance measurements of standard Ti solutions.

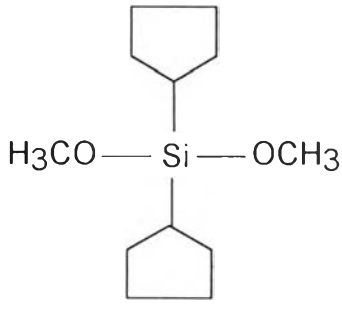
3.4 Experimental Procedure

Propylene polymerizations were performed in a 2-litre batch reactor under pressure 30-35 kg/cm^2 and temperature 70°C. $TiCl_4/MgCl_2$/dibutylphtalate-$Al(Et)_3$/external donor were used in the catalyst system. Polymerizations were done exactly the same way with external donor and no donor. Five different alkoxy silanes of structure $R_1R_2Si(OCH_3)_2$ where R_1, R_2 = aryl or alkyl, were used as external donors which are shown in Table 3.1. Figure 3.1 shows molecular structure of external donors.

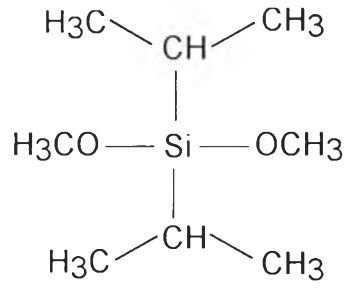
Table 3.1 Compounds used as external donors

Alkoxy silane	Code
Dicyclopentyldimethoxysilane	DCPDMS
Diisopropyldimethoxysilane	DIPDMS
Isobutylisopropyldimethoxysilane	IBIPDMS
Diisobutyldimethoxysilane	DIBDMS
Cyclohexylmethyldimethoxysilane	CHMDMS

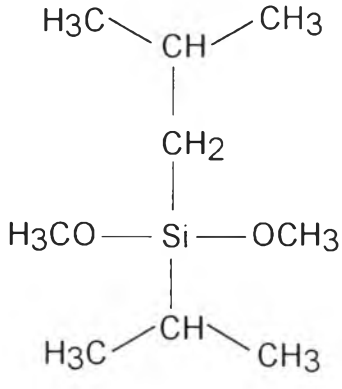
The influences of electron donor on the properties of polypropylene were investigated. The activity, melt flow rate, isotactic index, molecular weight, molecular weight distribution, melting and crystallization temperature, were characterized.



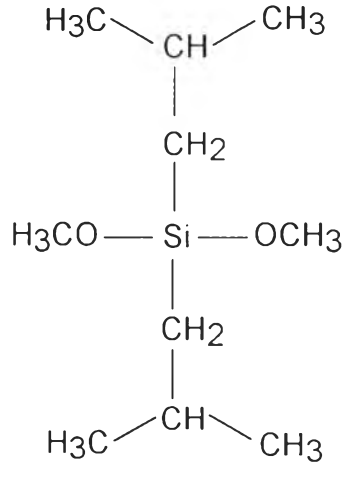
Dicyclopentyldimethoxysilane



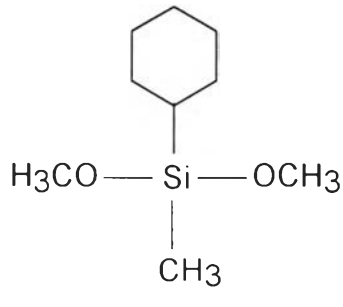
Diisopropyldimethoxysilane



isobutylisopropyldimethoxysilane



Diisobutyldimethoxysilane



Cyclohexylmethyldimethoxysilane

Figure 3.1 Molecular structure of external donors

3.5 Polymerization Procedure

Figure 3.2 shows process flow diagram of propylene polymerization reactor system.

Propylene polymerization was performed in a stainless steel jacketed reactor. Leakage of reactor was tested under pressure 40 kg/cm^2. The reactor was purged and dried by N_2 at 70°C for 1 h and cooled down to ambient temperature. The reactor was isolated under nitrogen atmosphere. The agitator was started at 100 rpm. The reactor vapor space was purged with propylene by repeated pressurization and depressurization. Five hundred grams of propylene was fed into the reactor by using a weight scale. After addition of hydrogen into the reactor at the desired pressure, agitator speed was increased to 750 rpm. Feed port was purged with nitrogen and opened. The desired quantity of hexane, external donor, triethylaluminum, and $MgCl_2$-supported titanium halide with diester catalyst were introduced by means of a pipette under dried N_2 into the feed port respectively. The feed port was closed, and pressure increased to 40 kg/cm^2 by using high-pressure nitrogen. The combined catalyst was fed into the reactor via the feed port at 60°C with starting timer. The polymerization time was 1 h and the temperature was 70°C. In order to stop the reaction, 5 mL. of ethanol was fed into the reactor via the feed port with decreasing agitator speed to 100 rpm. The reactor was cooled down to ambient temperature. The reactor was evacuated and purged with nitrogen for 1 hour after turning off agitator. The reactor was isolated and disassembled. The polymer powder was transferred from the reactor and dried in an oven under nitrogen atmosphere and then determined its weight.

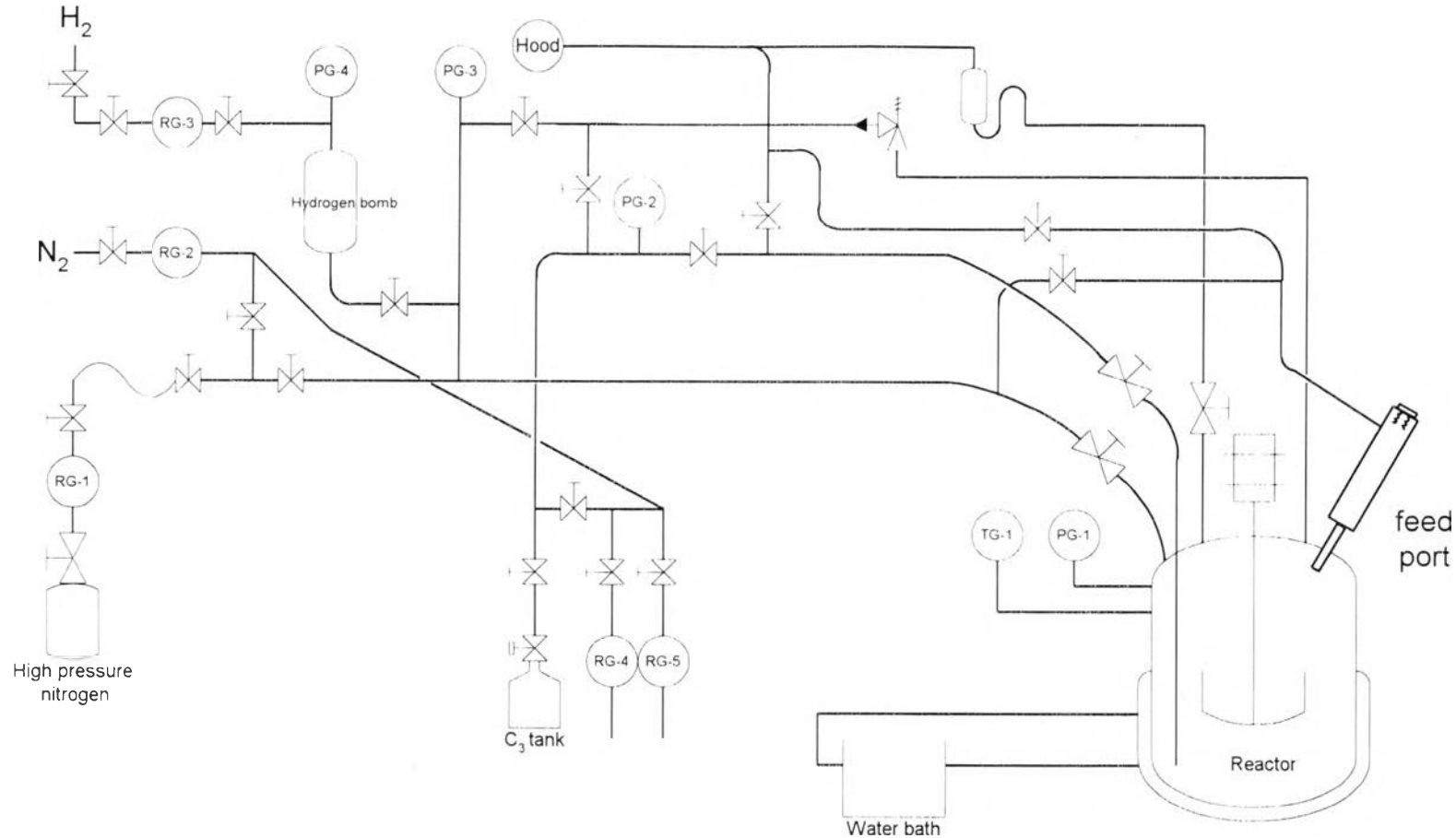


Figure 3.2 The process flow diagram of propylene polymerization reactor system.

3.6 Experimental Parameters

3.6.1 Fixed or Controlled Parameters

- Amount of catalyst (Ti is 0.003mM)
- Cocatalyst concentration (Al is 1000 mM/l)
- External donor concentration (De is 250 mM/l)
- Temperature (T is 70°C)
- Internal donor (di-n-butylphatalate)

3.6.2 Variable Parameters

- Types of external donors
  - DCPDMS
  - DIPDMS
  - IBIPDMS
  - DIBDMS
  - CHMDMS
- Amount of external donor (De/Al is 0.00, 0.05, 0.10, 0.20)
- Amount of cocatalyst (Al/Ti is 167, 333, 666)
- Amount of hydrogen (H_2 is 0.04, 0.07, 0.10 mol)

3.7 Melt Flow Rate

Melt flow rate (MFR) quoted for resins were determined by melt flow index tester, KAYENESS model 4000, of polypropylene polymer samples with referring to ASTM D 1238 in unit of g/10min. This test method covered measurement of the rate of extrusion of molten resins through a die of a specified length and diameter under prescribed conditions of temperature at 230°C, load 2.16 kg, piston position in the barrel, and 6 min preheating time.

3.8 Polymer Characterization

The molecular weight distributions of propylene polymers (the number-average and weight-average molecular weights) were determined by Gel Permeation Chromatography (GPC), a Waters Associates model: 150c ALC/GPC interfaced to an NEC Power Mate SX/16 microcomputer with referring to ASTM Standard: D3593. Samples of 0.0075 g were dissolved in 5 ml of o-dichlorobenzene after that the solution samples were heated to 145°C and filtered into vials and closed with Teflon lids. The solution samples were taken to the GPC holding sample case. The GPC was started by pushing the auto-inject button at temperature 145°C and the solvent flow rate 10 ml/min. Each solution of polypropylene sample was injected into a chromatographic column (series) packed with porous substrate. A separation was obtained according to polymer molecular size in solution. The size-separated molecules were detected by concentration-sensitive detector and recorded according to their concentrations.

3.9 Isotactic Index Determination

Soxhlet-type extraction with boiling solvent was used to determine the isotactic index of polypropylene samples with referring to MPC Standard: PPS108, as the following. The filter was weighed and approximately 3.0 g of the sample was placed into the filter and weighed. The filter that contains the sample was carefully placed in the Soxhlet-type extractor. After the addition of 200 ml n-heptane into the 300 ml flask, the flask was placed in the mantle heater. The Soxhlet extractor and the condenser were set on the top of the flask above the heater. The heater was turned on for the extraction of 3 hours. When the extraction was completed, the extractor and the condenser were

removed. The filter was taken out and dried in an oven under nitrogen atmosphere and weighed.

Calculation

Calculate isotactic index (II) of the sample as follows:

$$\text{Isotactic Index (\%)} = \frac{(C - A) * 100}{(B - A)}$$

where:

A = weight of the cylindrical filter

B = total weight of the cylindrical filter and the sample

C = total weight of the cylindrical filter and the sample after extraction.

3.10 Melting Temperature and Crystallization Temperature Determination

The melting temperature (T_m) and crystallization temperature (T_c) of polypropylene samples were determined by Differential Scanning Calorimeter (DSC), the Perkin Elmer Corporation model: DSC7 (with referring to MPC Standard: PPS137-2) as the following. Approximately 5 mg of the sample was weighed and put in the bottom of an aluminum pan. A lid was put on the aluminum pan and sealed with the sample sealer. An empty aluminum pan was prepared as a reference. The sample and reference were put on the DSC furnace. Approximately 50 mL/min of nitrogen gas was passed through the furnace of the equipment. The equipment was started to heat from 126°C to 180°C, using heating rate of 10°C/min. The T_m and T_c were determined from the chart obtained from the DSC.