CHAPTER III
EXPERIMENTAL

3.1 Introduction

In this research work ethylene propylene random copolymer was synthesized in a 2-litre batch reactor under pressure 30-35 kg/cm^2 and temperature 70°C. $TiCl_4/MgCl_2$/dibutylphtalate-$Al(Et)_3$/cyclohexylmethyldimethoxysilane were used in the catalysts system. The influences of electron donor and ethylene content on the properties of ethylene propylene random copolymer were investigated. The sample properties, isotactic index, molecular weight distribution, melting and crystalline temperature, were characterized.

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. Gel Permeation Chromatography (GPC) of Waters, model 150-C, for measuring the molecular weight of random ethylene propylene copolymer.
3. A Soxhlet-type extractor with a boiling solvent, for measuring isotactic index of random ethylene propylene copolymer.
4. Differential Scanning Calorimeter (DSC) of Perkin-Elmer, model DSC-7, for measuring the melting temperature and crystalline temperature of random ethylene propylene copolymer.

3.3 Raw Materials

Gas

- Nitrogen (ultra high purity grade) supplied by Thai Industrial Gas Co., Ltd. was used as received.
- Hydrogen (ultra high purity grade) supplied by Thai Industrial Gas Co., Ltd. was used as received.
- Ethylene (polymerization grade) supplied by National Petrochemical Public Co. was dried over molecular sieves.
- Propylene (polymerization grade) supplied by Thai Olefin Co., Ltd. was dried over molecular sieves.

Catalyst

- $MgCl_2$-supported titanium halide with dibutylphtalate catalyst.
- Triethylaluminum.
- Cyclohexylmethyldimethoxysilane.

Chemical

- Normal hexane supplied by Shell Chemicals Co., Ltd. was fractionally distilled before used.
- Ethanol supplied by Merck Co., Ltd. was used as received.

3.4 Polymerization Procedure

The schematic diagram of polymerization reactor is shown in Figure 3.1. The complete polymerization procedure was as follow:

1. The leakage of the reactor was tested under pressure 40 kg/cm^2
2. The reactor was purged with nitrogen for 1 hour. The temperature of the reactor was set at 70 ^oC, and pipette was purged with nitrogen for 10 minutes.

3. The reactor was cooled down to ambient temperature.
4. The reactor was isolated under nitrogen atmosphere.
5. The agitator was started at 100 rpm.
6. The reactor vapor space was purged with ethylene by repeated pressurization and depressurization.
7. The ethylene was fed into the reactor at the desired pressure.
8. 450 grams of propylene was fed into the reactor by using a weight scale.
9. Hydrogen was fed into the reactor at the desired pressure.
10. The agitation speed was increased to 450 rpm.
11. Feed port was purged with nitrogen and opened.
12. The desired quantity of hexane, cyclohexylmethyldimethoxysilane, triethylaluminum, and $MgCl_2$-supported titanium halide with diester catalyst was pipetted into the feed port respectively.
13. The feed port was closed and pressure increased to 35 kg/cm^2 by using high-pressure nitrogen.
14. The catalyst mix was fed into the reactor via the feed port at 60 ^oC and the timer was started.
15. The polymerization was continued for 1 hour at 70 ^oC.
16. 5 ml. of ethanol was fed into the reactor via the feed port in order to stop the reaction.
17. The agitator speed was decreased to 100 rpm.
18. The reactor was cooled down to ambient temperature.
19. The agitator was turned off.
20. The reactor was evacuated and purged with nitrogen for 1 hour.
21. The reactor was isolated and disassembled.
22. The powder was removed from the reactor.
23. The powder was dried in an oven under nitrogen atmosphere.

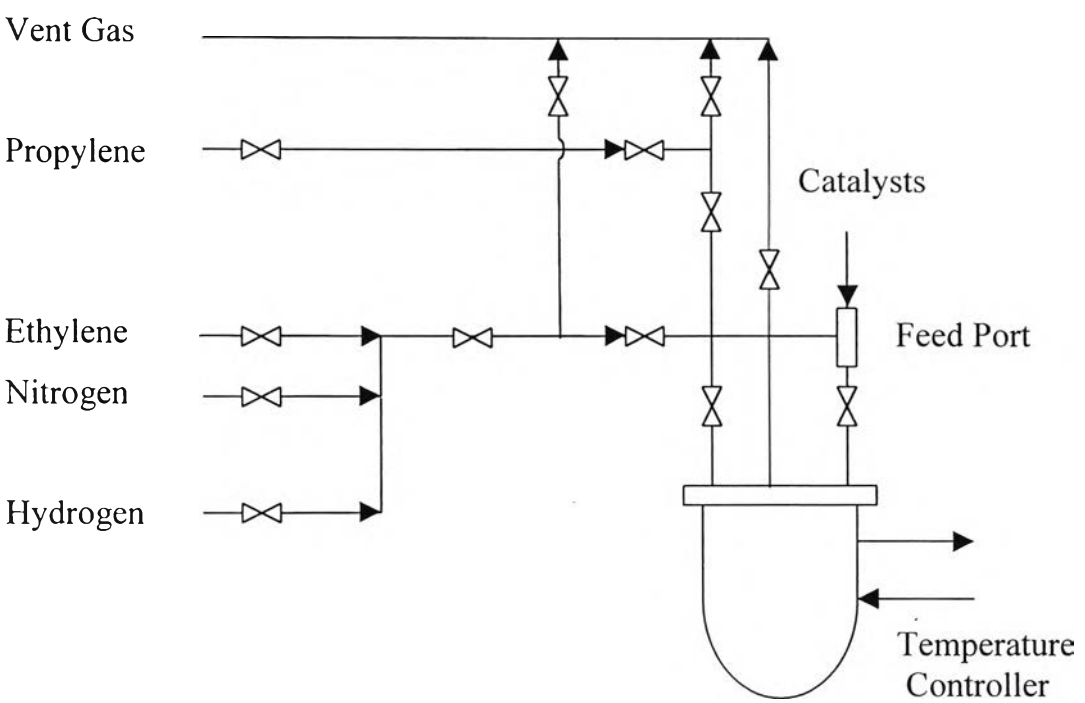

Figure 3.1 The schematic diagram of polymerization reactor system.

3.5 Molecular Weight Determination

The molecular weight of random ethylene propylene copolymer samples was determined by following The ASTM Standard: D3593. Gel Permeation Chromatography (GPC), A Waters Associates model: 150c ALC/GPC interfaced to an NEC Power Mate SX/16 microcomputer, was used as the following procedure:

1. 0.0075 g of sample was dissolved in 5 ml of o-dichlorobenzene.
2. The solution samples were heated to 145 ^{o}C and filtered into vials and closed with Teflon lids.
3. The solution samples were taken to the GPC holding sample case.
4. The temperature was set to 145 ^{o}C and the flow rate of solvent was set at 10ml/min.
5. The GPC was started by pushing the auto-inject button.

3.6 Isotactic Index Determination

The MPC Standard: PPS108 was used to determine the isotactic index of random ethylene propylene copolymer samples. Soxhlet-type extraction with boiling solvent was used as the following procedure:

1. The filter was weighed and approximately 3.0 g of the sample was placed into the filter and weighed.
2. The filter that contains the sample was gently placed in the Soxhlet-type extractor.
3. 200 ml. of n-heptane was poured into the 300 ml. flask and the flask was placed in the mantle heater.
4. The Soxhlet extractor and the condenser were set on the top of the flask above the heater.
5. The heater was turned on continually for extraction for 3 hours.

6. When the extraction was completed, the extractor was removed.
7. 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:

Isotactic Index (%) = (c-a)*100/(b-a)

Where:

a = Weight of the cylindrical filter (g).

b = Total weight of the cylindrical filter and the sample (g).

c = Total weight of the cylindrical filter and the sample after extraction(g).

3.7 Melting Temperature and Crystallization Temperature Determination

The MPC Standard: PPS137-2 was used to determine the melting temperature and crystalline temperature of random ethylene propylene copolymer samples. Differential Scanning Calorimeter (DSC), The Perkin Elmer Corporation model: DSC7, was used as the following procedure:

1. Approximately 5 mg. of the sample was weighed and put in the bottom of an aluminum pan.
2. A lid was put on the aluminum pan and sealed with the sample sealer.
3. An empty aluminum pan was prepared as a reference by following the same procedureThe sample and reference were taken to the DSC holding sample case.
4. Approximately 50 ml/min of nitrogen gas was passed through the furnace of the equipment.
5. The equipment was started to heat from 126 ^{o}C to 180 ^{o}C, using heating rate of 10 ^{o}C/min.
6. The Tm and Tc were determined from the chart obtained from the DSC.