

CHAPTER III

EXPERIMENTAL

3.1 Material and Chemicals

All manipulations involving air and moisture sensitive compounds were always carried out under dry nitrogen. Diethoxymagnesium (commercial grade, ethanol less than 2%, Degussa, Germany) and titanium tetrachloride (commercial grade, Ti oxide UK Limited, England) were used without further purification. Triethyl aluminium (TEA), (commercial grade, Crompton, Germany) was diluted by dried hexane. Aliphatic hydrocarbon (boiling range between 192 and 245 °C, Exxon Chemical Thailand Ltd., Thailand) was dried by refluxing in nitrogen over sodium metal and stored over 4 Å molecular sieves, Ethylene gas (polymerization grade, Thai Petrochemical Industry (publish), Thailand) and hydrogen gas (commercial grade, Thai Petrochemical Industry (publish), Thailand)

3.2 Instrument

Following are the list of major instrument used in this study.

1. MPX 62.92 Gottfert Melt Flow Indexer (MFI)
2. PL-GPC 220 high temperature chromatography (GPC)
3. Stainless steel reactor with stirrer for polymerization

3.3 Experimental

3.3.1 Preliminary Study of Catalyst Support Preparation

United States Patent number 5,648,309 was repeated. A suspension of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (57 g, 0.5 mol) in 500 ml aliphatic hydrocarbon was treated at 80, 85 or 90 °C with TiCl_4 by using 100, 350 or 450 stirring rate. After dropwise or one portion addition of TiCl_4 for 5.0 h, the catalyst support was washed, by decanting and stirring, each with 400 ml of aliphatic hydrocarbon at 70 °C or until Ti concentration in supernatant less than 10 mmol/L. The resulting product was allowed to room temperature and analyzed Mg, Ti and Cl concentration. The resulting product (200-ml) was treated with $\text{Al}(\text{C}_2\text{H}_5)_3$ at room temperature for 2 hours. The molar ratio $\text{Al}(\text{C}_2\text{H}_5)_3$: Ti in resulting suspension is 2. After analysis of total Ti and Ti(III) concentrations, these catalysts were used for initiation of ethylene polymerization and resulting polymers were characterized by MFI analysis. Table 3.1 and scheme 3.1 show different condition of catalyst support preparation and catalyst preparation procedure.

Table 3.1 Different condition of catalyst support preparation

Entry No.	Reaction temperature (°C)	Stirring rate (rpm)	TiCl_4 addition
1	80	350	Dropwise
2	85	350	Dropwise
3	90	350	Dropwise
4	85	100	Dropwise
5	85	350	One portion
6	85	450	Dropwise

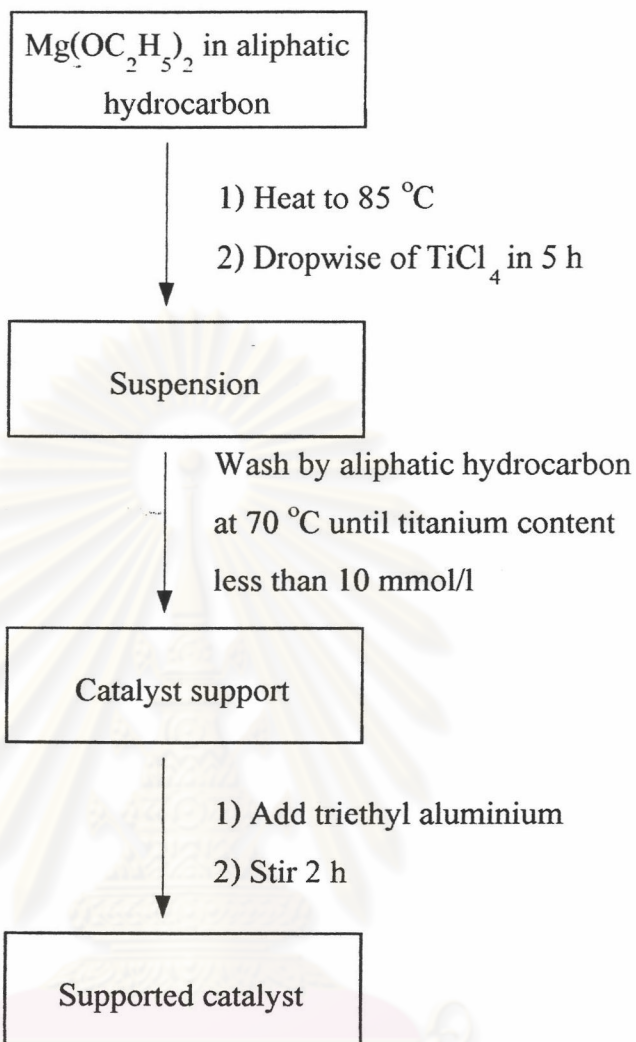


Figure 3.1 Catalyst preparation procedure in US. Patent No. 5,648,309 and used for producing low molecular weight HDPE

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3.3.2 Preparation of Z/N Catalyst for Producing Low Molecular Weight

HDPE

Preparations of these catalysts were performed according to Scheme 3.1. A suspension of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (57 g, 0.5 mol) in 500 ml aliphatic hydrocarbon was treated at 85 °C with TiCl_4 . Detailed experimental concentration data was summarized in Scheme 3.1 and Table 3.1. After dropwise of TiCl_4 for 5.0 h, the catalyst support was washed, by decanting and stirring, each with 400 ml of aliphatic hydrocarbon at 70 °C or until Ti concentration in supernatant less than 10 mmol/L. The resulting product was allowed to room temperature and analyzed Mg, Ti and Cl concentration. The resulting product (200-ml) was treated with $\text{Al}(\text{C}_2\text{H}_5)_3$ at room temperature for 2 hour. The molar ratio $\text{Al}(\text{C}_2\text{H}_5)_3$: Ti in resulting suspension is 2. After analysis of total Ti and Ti(III) concentrations, these catalysts were used for initiation of ethylene polymerization and resulting polymers were characterized by MFI analysis.

Table 3.2 A summary of chemical and metal concentration

Catalyst	$[\text{TiCl}_4] / [\text{Mg}(\text{OC}_2\text{H}_5)_2]$
R1	1.5
R2	2.0
R3	2.5
R4	3.0
R5	4.0

3.3.3 Preparation of Z/N Catalyst for Producing High Molecular Weight

HDPE

Preparations of these catalysts were performed according to Scheme 3.2. A suspension of $\text{Mg}(\text{OC}_2\text{H}_5)_2$ (57 g, 0.5 mol) in 500 ml aliphatic hydrocarbon was treated at 85 °C with TiCl_4 (138.6 ml, 1.25 mol). After dropwise of TiCl_4 for 5.0 hour, suspension 1 was washed by decanting and stirring, each with 400 ml of aliphatic hydrocarbon at 70 °C as 0, 1, 2, 3, 4 times or until Ti concentration in supernatant less than 10 mmol/L. Suspension 2 was heated to 120 °C and stirred for 2 hours. They were washed again until Ti concentration in supernatant less than 10 mmol/L. Catalyst support was allowed to room temperature and analyzed Mg, Ti and Cl concentration. After separation of resulting product in 2 parts, they were treated with $\text{Al}(\text{C}_2\text{H}_5)_3$ at room temperature and 120 °C for 2 h. respectively. The molar ratio $\text{Al}(\text{C}_2\text{H}_5)_3$: Ti in resulting suspension is 2. After analysis of total Ti and Ti(III) concentrations, these catalysts were used for initiation of ethylene polymerization and resulting polymers were characterized by MFI analysis.

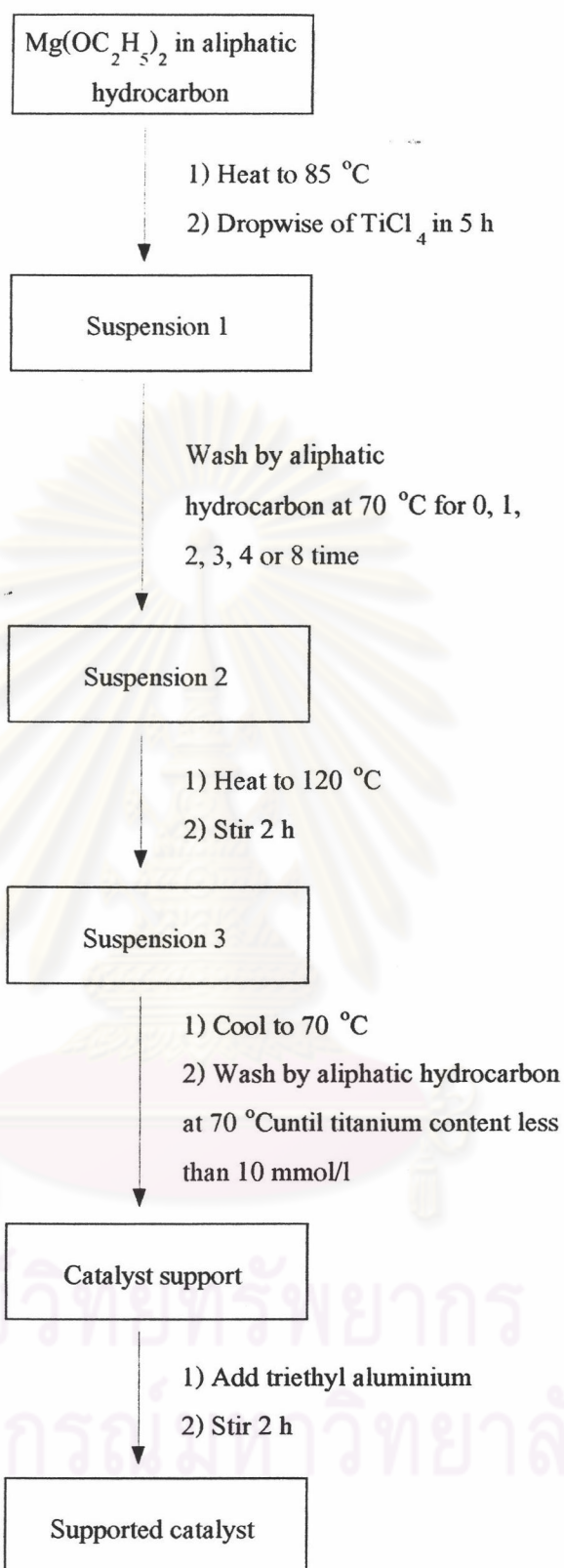


Figure 3.2 Catalyst preparation procedure for producing high molecular weight HDPE

3.3.4 Mixing of Catalyst

After consideration of polymer properties as MFI₅ and activity, selected catalysts were used for mixing by variation of Ti concentration of supported catalyst and initiated ethylene polymerization. The resulting polymers were characterized by MFI analysis and GPC technique.

3.4 Characterization of Catalyst and Polymer

3.4.1 Catalyst Characterization

Catalyst support and supported catalyst were analyzed after hydrolysis by diluted sulfuric acid. Three main elements were quantitatively analyzed as magnesium, titanium and chloride.

3.4.1.1 Quantitative Analysis of Total Ti

Catalyst support and supported catalyst were hydrolyzed by 1 mole/liter of H₂SO₄ and was reduced by shaking with zinc-amalgam for 10 minutes. After separation of zinc-amalgam, sample solution was titrated with 0.1 mole/liter cerium (IV)sulfate by using diphenylamine as indicator. End point of titration shows deep violet clear solution.

3.4.1.2 Quantitative Analysis of Ti(III)

Catalyst support and supported catalyst were hydrolyzed by 0.5 mole/liter of H₂SO₄. Sample solution was titrated with 0.1 mole/liter cerium(IV)sulfate by using diphenylamine as indicator. End point of titration shows deep violet clear solution.

3.4.1.3 Quantitative Analysis of Magnesium and Chloride

Catalyst support and supported catalyst were hydrolyzed by 3 mol/L of H_2SO_4 . Organic medium was separated from sample solution. Sample solution was made volume to 250 milliliter and was pH adjusted in range of 4-6. After filtering of titanium hydroxide precipitate, sample solution was made volume to 500 milliliter. It was separated in 2 parts. First part was quantitatively analyzed of magnesium following ASTM D511-88.^[13] Second part was quantitatively analyzed of chloride following ASTM D512-88.^[14]

3.4.2 Polymerization Procedure

The polymerization reactions were carried out in a 1.5-liter reactor equipped with a mechanical stirrer. The reactor was filled with 750 ml dried hexane, $\text{Al}(\text{C}_2\text{H}_5)_3$ and the catalyst (molar ratio $\text{Al}(\text{C}_2\text{H}_5)_3 : \text{Ti} = 100$). The reactor was heated to 85°C and it was pressurized with 2.85 bar hydrogen and 3.15 bar ethylene. The pressure was kept constant during polymerization by ethylene flowrate control. The polymerization was stopped after 2 hours by shutting off ethylene valve and cooling to room temperature. The resulting polymer-suspension was filtered and dried at 80°C in oven.

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2.2.3 Polymer Characterization

Melt flow indexes were determined with a MPX 62.92 Gottfert Melt Flow Indexer at 190 °C according to the ASTM D 1238 method.^[19] The test load for MFI₅ and MFI_{21.6} were 5 and 21.6 kg respectively. Melt flow ratio (MFR) was defined by ratio of MFI_{21.6} with MFI₅.

Molecular weight by weight (Mw) and MWD of the polymers were measured using a PL-GPC high temperature chromatography with a differential reflective index detector and a viscometric detector. The polymer sample were dissolved in o-dichlorobenzene (ODCB) at a concentration of 0.02 wt % and measured at 135 °C with a flow rate of 1 ml/min. The GPC was equipped with two linear crosslinked polystyrene columns (PLgel: Mixed-B). The retention times were calibrated at 135 °C against known monodisperse TSK polystyrene standards from TOYO SODA Mfg. Co.

