CHAPTER IV

EXPERIMENT

In the present study of the styrene polymerization with homogeneous and heterogeneous titanocene catalysts, the experiment was divided into:

1. Synthesis and characterization of titanocene catalysts and polymer-supported titanocene catalysts
2. Styrene polymerization with the prepared catalysts
3. Characterizations of polystyrene product

4.1. Chemicals

The chemicals used in this experiment were analytical grade.

Chemicals	Suppliers
Ultra high purity nitrogen gas (99.999%)	Thai Industry Gas Co., Ltd., Thailand
Styrene monomer (density 0.906 g/cm^3)	Fluka Chemie A.G., Switzerland
Cyclopentadienyltitanium trichloride, CpTiCl$_3$	Fluka Chemie A.G., Switzerland
Pentamethylcyclopentadienyltitanium trichloride, Cp*TiCl$_3$	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
Tris(pentaflurophenyl)boron, B(C$_6$F$_5$)$_3$	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
Triphenylcarbenium tetrakis (pentafluorophenyl)borate, [Ph$_3$C][B(C$_6$F$_5$)$_4$]	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan

Dimethylanilinium tetrakis (pentafluorophenyl)borate, $[PhNMe_2H][B(C_6F_5)_4]$	Donated from Dow Chemical, USA
Triisobutylaluminium (TIBA)	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
Methylaluminoxane (MAO)	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
Merrifield polymer (crosslinked with 2% DVB); 4.3 mmol Cl/g resin	Fluka Chemie A.G., Switzerland
Dimethylamine	Aldrich Chemical Co., Inc., USA
Toluene	Fluka Chemie A.G., Switzerland
Methyl ethyl ketone (MEK)	Carlo Erba, Italy

Many of the reagents in this work react violently with water and ignite spontaneously in air (by reaction with oxygen and/or moisture). These chemicals were handled safely under inert atmosphere by Schlenk and glove bag techniques. All chemicals and solvents were dried before use as following methods:

1.   Ultra high purity nitrogen gas was purified by passing through three columns packed with molecular sieve 4°A, NaOH and P_2O_5, respectively.

2.   Toluene was purified by refluxing over sodium/benzophenone and distilled under nitrogen atmosphere before use.

3.   Styrene monomer containing inhibitor, was removed inhibitor by washing with 10% aqueous sodium hydroxide and subsequently demineralised water until the pH of aqueous phase was neutral. After being dried over anhydrous magnesium sulfate, 0.5 g CaH_2 was added to inhibitor-free styrene monomer. Then it was distilled under reduced pressure. The styrene monomer was collected and dissolved oxygen was removed by purging nitrogen gas through.

4.   Dichloromethane was purified by refluxing over CaH_2 and distilled under nitrogen atmosphere before use.

4.2.   Equipments

All equipments, used in the catalyst preparation and polymerization, were listed as follows:

4.2.1.   Schlenk line

Schlenk line (Figure 4.1) consists of nitrogen and vacuum line. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap and the oil bubbler containing enough oil to provide a seal from the atmosphere when nitrogen line was evacuated.
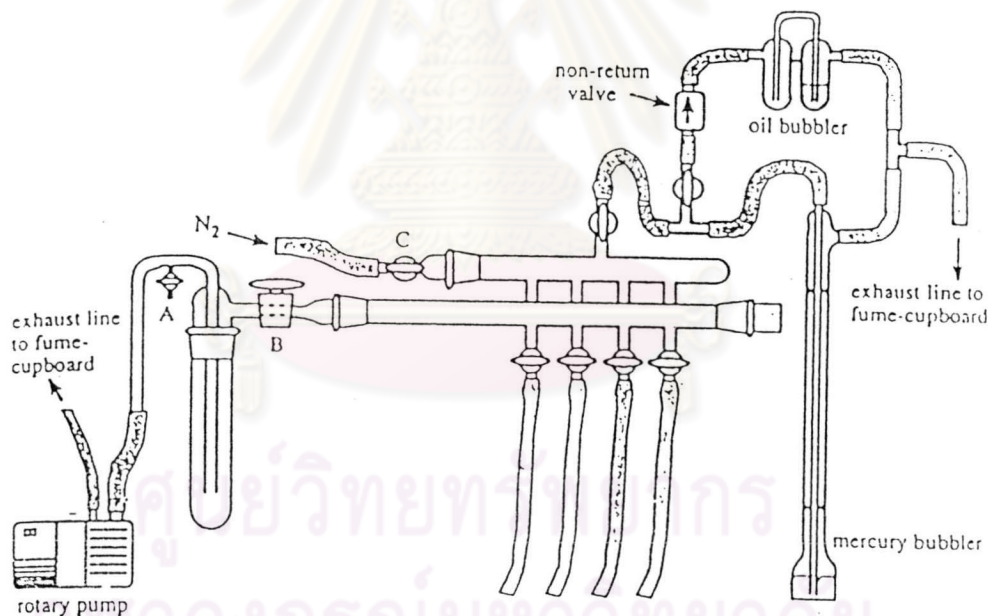

Figure 4.1. Schlenk line.

4.2.2.   Heating bath

The oil bath with thermometer was used to control the temperature of polymerization reaction.

4.2.3. Vacuum pump

A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.

4.2.4. Schlenk flask

A flask with a side-arm is used with inert gas (Figure 4.2). A joint to connect to other items of glassware provides access to the contents, and a tab for connection to the manifold.
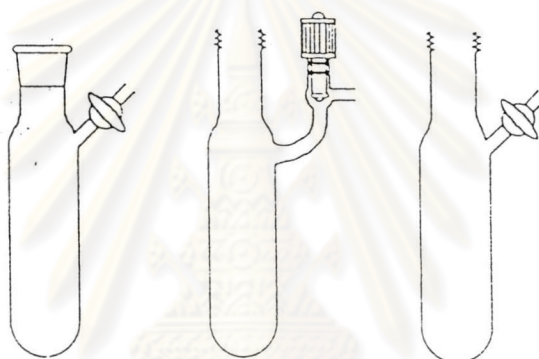
Figure 4.2. Round-bottomed and tube designs for Schlenk flasks incorporating ground–glass joints.

4.2.5. Inert gas supply

The inert nitrogen gas from cylinder was passed through drying column with $4A°$ molecular sieves. The inert gas was used to feed in the nitrogen line of Schlenk line and polymerization reactor.

4.2.6. Syringe and needle

The syringes with volume of 5, 10, 50 mL, needles No 19, 20, 22 were used.

4.2.7. Glove bag

Glove bag is a moderate-volume gas-tight container from which air or moisture is excluded. The glove bag has a way to connect with Schlenk line, which can be evacuated and then filled with nitrogen.

4.2.8. Vacuum oven

Polymer was dried at 60°C under vacuum oven until weight constant.

4.2.9. Soxhlet extractor

Soxhlet extractor (Figure 4.3) was used for determining syndiotactic content. Polystyrene product was weighted in a cellulose thimble, and then was extracted with methyl ethyl ketone for 5 hours. The residual polymer was dried at 80°C in vacuum oven until constant weight. The fraction of the whole polymer unextracted and multiplied by 100 was taken as a percent of syndiotactic polystyrene (%SPS).
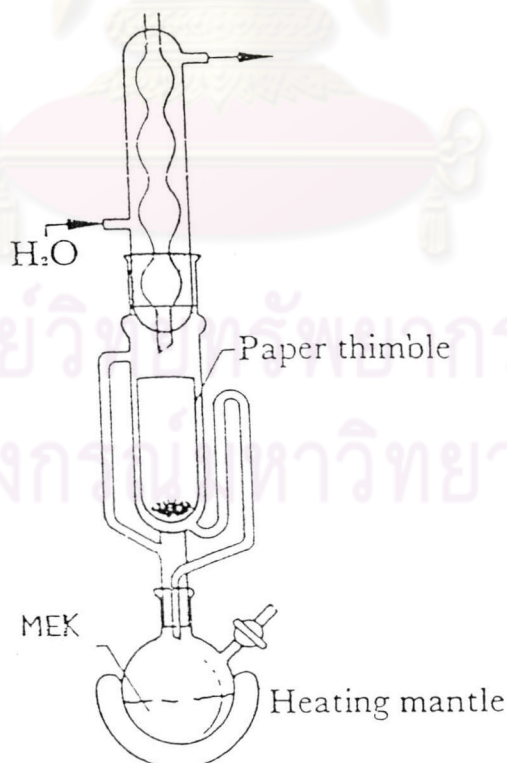

Figure 4.3. Soxhlet-type extractor.

4.3.   Characterization instruments

The instruments used to characterize catalysts and polystyrene were specified in the following.

4.3.1.   Fourier transform infrared spectrometer (FT-IR)

Nicolet FT-IR impact 410 spectrophotometer at Chemistry Department, Chulalongkorn University, was employed to characterize catalysts. Infrared spectra were recorded between 400 and 4000 cm^{-1} in transmittance mode.

4.3.2.   Gel permeation chromatograph (GPC)

Molecular weight and molecular weight distribution of the produced polystyrene were measured at 135°C using 1,2,4-trichlorobenzene as solvent at 1.0 ml/min by a Waters 150-C column. GPC curves of polystyrene were determined at Chemical Resources Laboratory, Tokyo Institute of Technology, Japan.

4.3.3.   Differential scanning calorimeter (DSC)

The glass transition temperature (T_g) and melting temperature (T_m) of polystyrene was determined by a NETZSCH DSC 200 at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The analyses were performed at the heating rate of 10°C/min. in the temperature range of 25-300°C. The heating cycle was run twice. In the first scan, samples were heated and then cooled down to room temperature. In the second scan, samples were reheated at the same rate, only the second scan was recorded because the first scan was influenced by the mechanical and thermal history of samples.

4.3.4. Nuclear magnetic resonance spectroscopy (NMR)

^{13}C-NMR spectra of polystyrene were recorded on JEOL JNM-A500 at Chemical Resources Laboratory, Tokyo Institute of Technology, Japan.

4.3.5. Scanning electron microscope (SEM)

Morphology of the polymer bead and polymer products were recorded on JEOL JSM-5800 LV at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

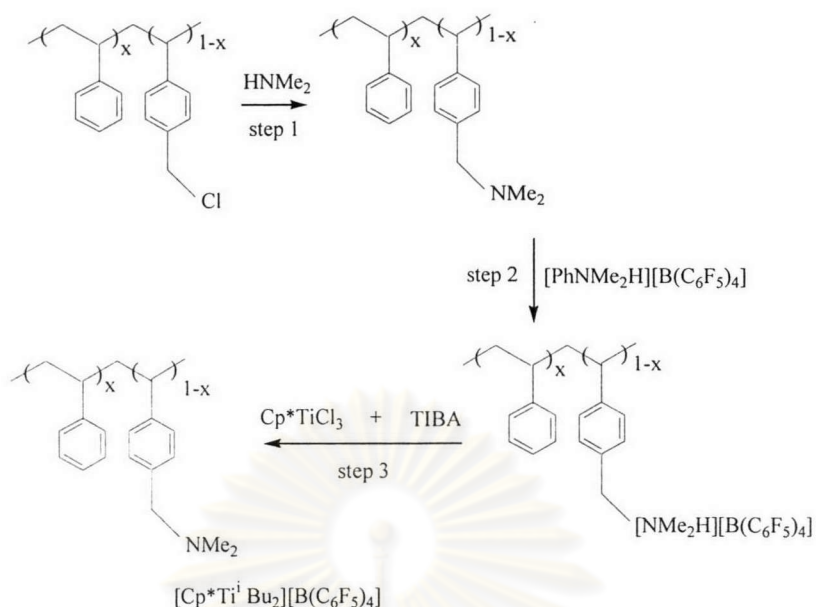## 4.4. Synthesis of polymer-supported titanocene catalysts.

All operations were performed under nitrogen atmosphere by using Schlenk techniques.

4.4.1. Boron compound as cocatalyst

There are two types of titanocene catalyst used in preparation of polymer-supported catalyst: Cp*TiCl$_3$, CpTiCl$_3$. Supported catalyst was prepared by treating crosslinked chloromethylated polystyrene beads with a secondary amine (step 1), an ammonium salt of a weakly coordination anion (step 2), and finally a metallocene (step 3) (Figure 4.4). The details of three steps were as follows:

Preparation of alkyl titanocene

A prescribed amount of Cp*TiCl$_3$ in toluene was mixed with prescribed amount of triisobutylaluminum (TIBA) in toluene and then the mixture was preactivated for 1 h at room temperature.

Figure 4.4. Synthesis of polymer-supported catalyst using boron compound as cocatalyst.

Step 1. Synthesis of PS-CH$_2$NMe$_2$

In a 100 mL Schlenk flask with a magnetic stirring bar, chloromethylated polystyrene-*co*-DVB beads (0.07 g, 4.3 mmol Cl/g resin) were swollen in a 2 M solution of dimethylamine in THF (10 mL) and stirred for 2 days at room temperature. The beads were filtered and rinsed with THF and water.

Step 2. Synthesis of PS-CH$_2$[NMe$_2$H][B(C$_6$F$_5$)$_4$]

The aminated beads (0.07 g) in 100 mL Schlenk flask were treated with a solution of [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (0.24 g, 1 equivalent with respect to dimethylamine (in step 1)) in dichloromethane (20 mL) for 2 h and then filtered and rinsed with dichloromethane.

Step 3. Synthesis of PS-CH$_2$NMe$_2$: [B(C$_6$F$_5$)$_4$] [Cp*TiBu$_2$]

The solution of Cp*TiCl$_3$ + TIBA was added to the 0.07 g of the borated dimethylamine-functionalized beads. The mixture was stirred for 1 h at room temperature and then the beads were filtered and rinsed with toluene.

4.4.2. MAO as cocatalyst

Two methods were performed to synthesize polymer-supported catalyst using MAO as cocatalyst.

Method A: There are two types of titanocene catalyst used in preparation of polymer-supported catalyst: Cp*TiCl$_3$, CpTiCl$_3$. Supported catalyst was prepared by treating crosslinked, chloromethylated polystyrene beads with a secondary amine (step1), MAO (step 2), and a metallocene (step 3) (Figure 4.5). The details of three steps were as follows:
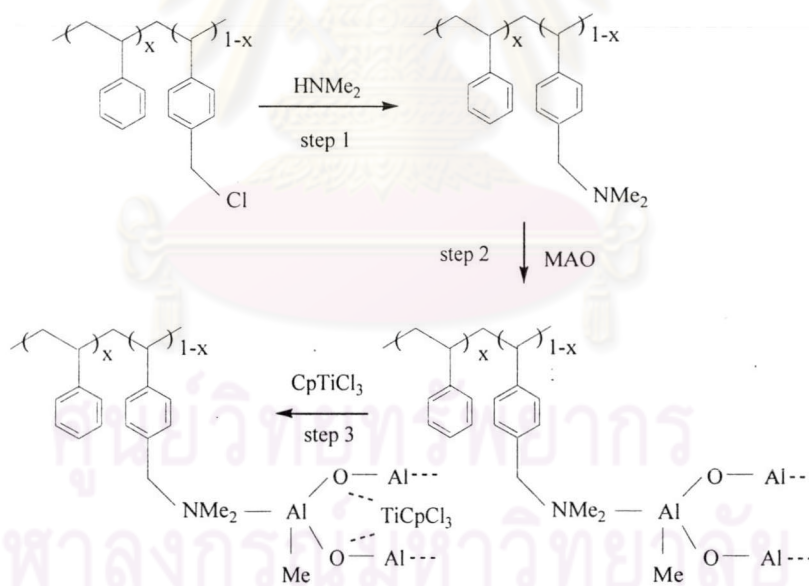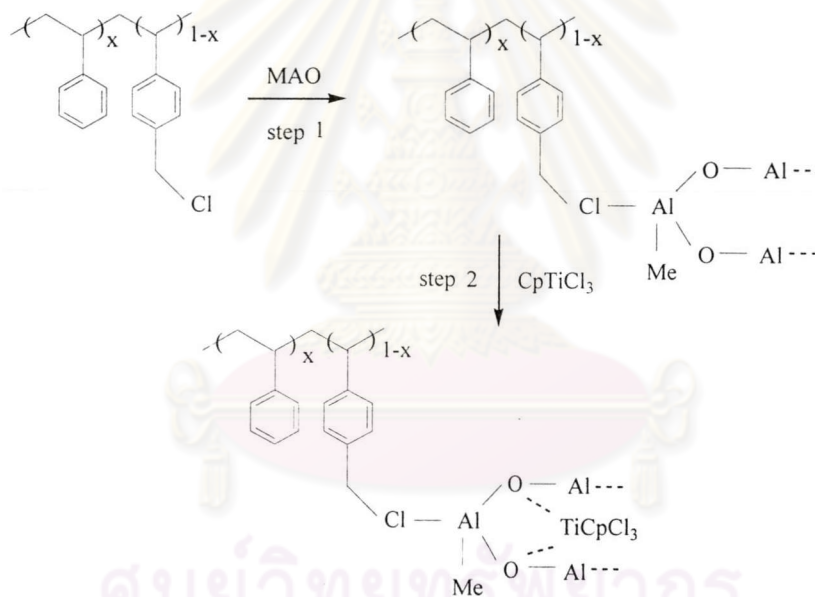
Figure 4.5. Synthesis of polymer-supported catalyst using MAO as cocatalyst (method A).

Step 1. It is same as in 4.4.1.

Step 2. Polystyrene-*co*-DVB beads (0.10 g) were swollen in toluene (20 mL) and stirred for 15 min at room temperature and then a 3 mmol of MAO was added and stirred for 4 h at room temperature. The beads were filtered and rinsed with toluene.

Step 3. A prescribed amount of $CpTiCl_3$ in toluene was added to the 0.10 g of polystyrene-*co*-DVB beads. The mixture was stirred for 24 h at 50°C and then the final supported catalyst was collected after filtration and washed with toluene.

Method B: Supported catalyst was prepared by treating crosslinked, chloromethylated polystyrene beads with MAO (step 1), and metallocene (step 2) (Figure 4.6). The details of two steps were as follows:

Figure 4.6. Synthesis of polymer-supported catalyst using MAO as cocatalyst (method B).

Step 1. Chloromethylated polystyrene-*co*-DVB beads (0.10 g, 4.3 mmol Cl/ g resin) were swollen in toluene (20 mL) and stirred for 15 min at room temperature and then a 3 mmol of MAO was added and stirred for 4 h at room temperature. The beads were filtered and rinsed with toluene.

Step 2. It is same as step 3 in method A.

4.5. Catalyst and cocatalyst solution preparation

1. CpTiCl$_3$, Cp*TiCl$_3$ 20 mg was dissolved in 30 mL of toluene.

2. B(C$_6$F$_5$)$_3$, [Ph$_3$C][B(C$_6$F$_5$)$_4$], [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] 40 mg was dissolved in 30 mL of toluene.

3. TIBA 12.6 mL was dissolved in 87.4 mL of toluene under nitrogen atmosphere to get 0.5 molar concentration.

4.6. Polymerization procedure

4.6.1. Homogeneous system

4.6.1.1. Polymerization of styrene with CpTiCl$_3$/MAO system

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. A prescribed amount of MAO, styrene (87 mmol, 10 mL) and 0.0100 mmol of CpTiCl$_3$ in toluene (40 mL) were added in that order. The reaction mixture was stirred for 4 h at a certain temperature. The polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight.

4.6.1.2. Polymerization of styrene with Cp*TiCl$_3$/TIBA/boron compound system

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. A prescribed amount of Cp*TiCl$_3$ in toluene was mixed with prescribed amount of triisobutylaluminium (TIBA) in toluene and then the mixture was preactivated for 15 min at room temperature. A prescribed amount of boron cocatalyst, styrene (87 mmol, 10 mL) were added to the mixture and stirred for 1 h at 70°C. The polymerization was terminated by the addition of 10%

HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight.

The effect of type of boron compounds was investigated: ($B(C_6F_5)_3$, [Ph_3C][$B(C_6F_5)_4$] and [$PhNMe_2H$][$B(C_6F_5)_4$]).

4.6.2. Heterogeneous system

4.6.2.1. Polymerization of styrene using boron compound as cocatalyst

4.6.2.1.1. Polymer-supported Cp*TiCl₃ catalyst

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. Styrene (87 mmol, 10 mL) was added to the 0.07 g of polymer-supported Cp*TiCl₃ catalyst. The mixture was stirred for 4 h at a certain temperature. The polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight.

The effect of amount of catalyst

The amounts of catalyst were varied from 0.0050 to 0.1000 mmol. The polymerization was carried out for 4 h at 70°C, Al/Ti molar ratio of 200.

The effect of polymerization temperature

Polymerization temperatures were varied at 30 and 70°C. The polymerization was carried out for 4 h, Al/Ti molar ratio of 200, 0.0500 mmol of Ti.

The effect of Al/Ti molar ratio

The Al/Ti molar ratios were varied at 100 and 200. The polymerization was carried out for 4 h at 70°C, 0.1000 mmol of Ti.

4.6.2.1.2. Polymer-supported CpTiCl₃ catalyst

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. Styrene (87 mmol, 10 mL) was added to the 0.07 g of polymer-supported CpTiCl₃ catalyst. The mixture was stirred for 4 h at 70°C. The polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight.

4.6.2.1.3. Test of catalyst leaching from polymer support

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. A 0.10 g of polymer-supported Cp*TiCl₃ catalyst was swollen in toluene (20 mL) and stirred for 24 h at room temperature. The mixture was filtered and then the solid and liquid portions were used to catalyze the styrene polymerization for 4 h at 70°C. The polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight.

4.6.2.2. Polymerization of styrene using MAO as cocatalyst

4.6.2.2.1. Polymerization procedure

4.6.2.2.1.1. Polymer-supported titanocene catalyst/MAO system

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. Styrene (87 mmol, 10 mL) and MAO (3 mmol, 0.66 mL) were added to the 0.10 g of polymer-supported CpTiCl₃ catalyst. The mixture was stirred for 4 h at a certain temperature. The polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight.

4.6.2.2.1.2. Polymer-supported titanocene catalyst system

The polymerization was performed under nitrogen atmosphere in a 100 mL Schlenk flask with a magnetic stirring bar. Styrene (87 mmol, 10 mL) was added to the 0.10 g of polymer-supported $CpTiCl_3$ catalyst. The mixture was stirred for 4 h at 50°C. The polymerization was terminated by the addition of 10% HCl in methanol. The polymer was collected by filtration and washed several times with methanol, dried at 60°C in vacuum oven until constant weight

4.6.2.2.2. Polymer-supported $CpTiCl_3$ catalyst/MAO system (method A).

It is same as polymerization procedure in 4.6.2.2.1.1.

The effect of amount of catalyst

The amounts of catalyst were varied from 0.0100 to 0.1000 mmol. The polymerization was carried out for 4 h at 50°C, Al/Ti molar ratio of 300.

The effect of polymerization temperature

Polymerization temperatures were varied at 50 and 70°C. The polymerization were carried out for 4 h, Al/Ti molar ratio of 300, 0.1000 mmol of Ti.

4.6.2.2.3. Polymer-supported $CpTiCl_3$ catalyst system (method A).

It is same as polymerization procedure in 4.6.2.2.1.2.

4.6.2.2.4. Polymerization of styrene with polymer-supported $Cp*TiCl_3$ catalyst/MAO system (method A).

It is same as polymerization procedure in 4.6.2.2.1.1.

4.6.2.2.5. Polymerization of styrene with polymer-supported CpTiCl₃ catalyst/MAO system (method B).

It is same as polymerization procedure in 4.6.2.2.1.1.

4.7 Catalyst characterization

The infrared spectroscopy was used to follow each step in preparation of polymer supported catalyst. IR spectrum was compared to that from reference data.

4.8 Characterization of the polystyrene

In this work, polystyrene products were characterized by the following methods.

1. Gel permeation chromatograph (GPC)

Gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography (SEC) was used to determine molecular weight (M_w) and molecular weight distribution (MWD). Molecular weight and molecular weight distribution of the produced polystyrene were measured at 135°C using 1,2,4-trichlorobenzene as solvent at 1.0 mL/min.

2. Differential scanning calorimeter (DSC)

Differential scanning calorimeter (DSC) was used to measure melting temperature (T_m) and glass transition temperature (T_g) of the polystyrene.

3. Nuclear magnetic resonance spectroscopy (NMR)

Nuclear Magnetic Resonance Spectroscopy (NMR) was used to investigate the chemical structure of polymer. ^{13}C-NMR spectra illustrated carbon nucleus that each had its own electronic environment and showed the different chemical shift. The

chemical shift reflected the electronic environment of carbon. The coupling constant, J, was defined to the distance between peaks in a multiplet, a measure of the effectiveness of spin-spin coupling.

4. Scanning electron microscope (SEM)

Scanning electron microscope (SEM) was used to determine morphology of polymer bead and polymer product.

5. Syndiotacticity

The syndiotacticity content of polystyrene can be determined in a number of ways. The most widely used method involved extracting the polymer in a Soxhlet extractor with a methyl ethyl ketone. The fraction of the polystyrene unextracted multiplied by 100 was a percent of syndiotacticity.