

CHAPTER IV

EXPERIMENT

In the present study of the styrene polymerization on half-metallocene catalyst with methylaluminumoxane as cocatalysts, the experiments were divided into six parts.

1. Synthesis and preparation of catalyst
2. Cocatalyst preparation
3. Styrene polymerization with trimethylaluminium
4. Styrene polymerization with the prepared catalyst system
5. Characterization of polymer products
6. Characterization of catalyst

The details of the experiment were explained in the following.

4.1. Chemicals

The chemicals used in this experiment were normal analytical grade, but only critical materials had to be specified as follows.

1. Commercial methylaluminumoxane 1.4675 M. in toluene was donated by Nippon Aluminum Alkyls Ltd., Japan and used as received.

2. Ultra high purity nitrogen gas (99.999%vol.) with oxygen and moisture content less than 3 ppm. was supplied by Thai Industrial Gas Co. Ltd. and was purified by passing through the column packed with molecular sieve 4 Å to remove traces of moisture.

3. Aluminum Sulfate octahydrate $[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ was manufactured by Merck Ltd., Germany.

4. n-butyllithium obtained from Merck, Germany was used as received.

5. Indene (98%) was supplied by Fluka Chemie A. G. Switzerland. Indene was purified by distillation in vacuum before use.

6. Trimethylaluminum $[\text{Al}(\text{CH}_3)_3]$ 2 M. in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan and used without purification.

7. Pentane purchased from J. T. Baker, USA. was refluxed over sodium/benzophenone and freshly distilled prior to use.

8. Toluene was donated by Esso Chemical Co. Ltd. (Thailand). It was purified by passing through CaCl_2 and molecular sieve (4 Å) packed column and was refluxed over sodium/benzophenone and distilled under nitrogen atmosphere before use.

9. Tetrahydrofuran supplied from Carlo Erba, Italy was distilled from sodium/benzophenone under nitrogen atmosphere just before use.

10. Trimethylchlorosilane was obtained from Fluka Chemie A.G., Switzerland and used without further treatment.

11. CH_2Cl_2 was purchased from Lab Scans Ltd., IRELAND and used as received.

12. Titanium tetrachloride supplied from Carlo Erba, Italy was used without further purification.

13. Styrene monomer purchased from Fluka Chemie A.G., Switzerland was used as received.

14. Methyl ethyl ketone purchased from Carlo Erba, Italy was used without further treatment.

15. Methanol obtained from Carlo Erba, Italy was used as received.

4.2. Equipment

All equipment, used in the catalyst synthesis and polymerization, consisted of

1. Schlenk line

Schlenk line consists of nitrogen and vacuum line. The vacuum line is equipped with the solvent trap and pump, respectively. The nitrogen lines is connected to the trap and the mercury bubbler that was a manometer tube and contain enough mercury to provide a seal from the atmosphere when nitrogen line is evacuated. The schlenk line is shown in Figure 4.1.

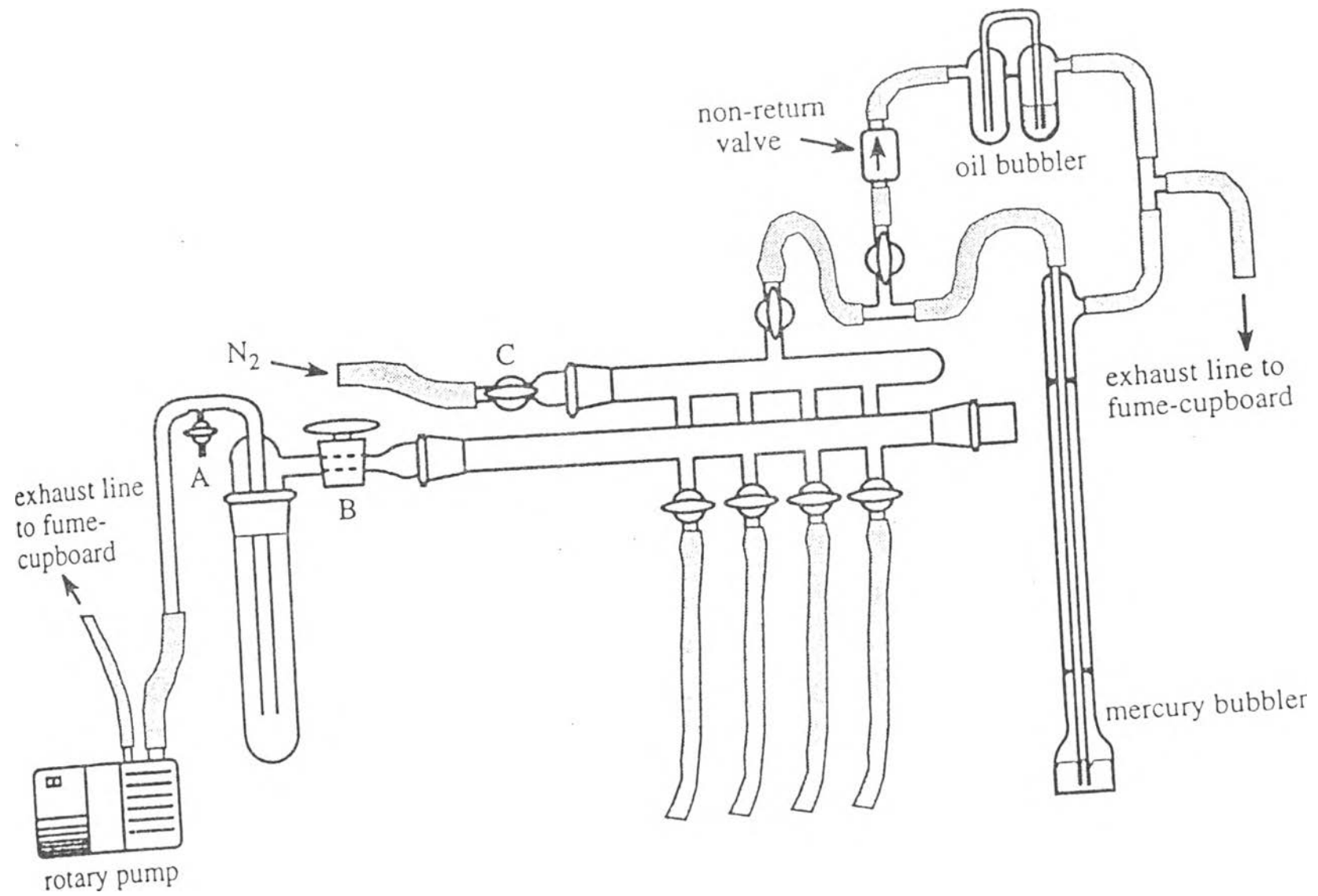


Figure 4.1. Schlenk line

2. Glass Reactor

The polymerization reactor was a 250 ml. modified glass bottle with a cap having a septum for injection. The reactor was equipped with several fittings for nitrogen and outlet lines.

3. Magnetic Stirrer and Hot Plate

The magnetic stirrer and hot plate model RCT basic from KJKA labortechnik were used.

4. Cooling System

The cooling system was used in the solvent distillation for condensing the freshly evaporated solvent. In the preparation of methylaluminumoxane cocatalyst, it was used to control temperature of reactor at constant 5°C.

5. Vacuum pump

A pressure of 10^{-2} to 10^{-3} mmHg is adequate for the vacuum supply to the vacuum line in a schlenk line.

6. The inert gas supply

The inert gas (normally nitrogen or argon) is passed through drying column with 4 Å molecular sieves. The inert gas is used to feed in the nitrogen line of schlenk line and the polymerization reactor.

7. Glove bag

Glove bag is a moderate-volume gas-tight container from which oxygen and/or moisture are excluded (in reality they are kept at very low levels). The glove bag has a three ways valve, which can be evacuated and then filled with nitrogen.

8. Syringe, Needle and Septum

The syringe used in the experiment had a volume of 50, 20, 10, 2, 1 cc. and needle were No. 15, 20 and 22, 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. Solvents, catalyst and cocatalyst were transferred to a glass bottle by using needles with a septum.

4.3. Characterization instruments

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

1. Soxhlet extractor

Soxhlet extractor was used for determining syndiotactic content. Polystyrene product was weighed in cellulose thimble about 0.1 g, and then was extracted with 2-butanone for 12 hours in nitrogen atmosphere. The residual polymer was dried at 110°C. The fraction of the whole polymer unextracted and multiply by 100 was taken as a percent of syndiotactic polystyrene (%sPS) according to the equation.

$$\%sPS = \frac{\text{Insoluble weight of polystyrene}}{\text{Total weight of polystyrene}} \times 100$$

2. Nuclear Magnetic Resonance Spectroscopy (NMR)

NMR is one of the most powerful tools available to the chemist and biochemist for elucidating the structure of both organic and inorganic species. NMR is based upon the measurement of absorption of electromagnetic radiation in the radio-frequency region of roughly 4 to 600 MHz. ¹H or ¹³C NMR spectra were recorded on JEOL JNM-A500 Nuclear Magnetic Resonance Spectrometer at Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. Spectra were referenced to 0 ppm for trimethylsilane-d₆ and 7.26 ppm

for deuteriochloroform. Chemical shifts were given in parts per million (ppm) and coupling constants (J) are in Hertz (Hz).

3. Electron Spin Resonance (ESR)

Electron Spin Resonance spectrum of the catalyst was conducted by using JEOL, JES-RE 2X Electron Spin Resonance Spectrometer at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University.

4. Fourier Transformed Infrared Spectroscopy (FT-IR)

NICOLET FT-IR Impact 400 spectroscopy at Petrochemical Engineering Research Laboratory, Chulalongkorn University, was employed to study the microstructure of polystyrene. Infrared spectra were recorded between 2000 and 400 cm^{-1} on a microcomputer.

4.4. Synthesis of catalyst

All operation were performed under nitrogen atmosphere by using Schlenk Lines and glove bag.

The synthesis of indenyltitanium trichloride

A solution of n-butyllithium 1.6M in hexane (0.085 mol) was slowly added to a solution of 10 g (0.085 mol) indene in 120 ml. THF cooled to -40°C . The reaction mixture was allowed to warm to room temperature and was stirred for 2 hrs. The reaction mixture (1-indenyllithium) was added to a solution of trimethylchlorosilane (0.085mol) in 20 ml. THF cooled to -40°C . A precipitate formed immediately. The THF solvent was then removed via a vacuum to a cold trap held at -196°C . The residue was extracted with pentane and filtered through celite. The solvent was removed from filtrate to give the product as a light-yellow oil (1-trimethylsilylindene).

1-trimethylsilylindene was added dropwise to a solution of TiCl_4 (0.085 mol) in 100 ml. of dichloromethane (CH_2Cl_2) cooled at -40°C . The resulting mixture was allowed to stir overnight and store at -20°C for 24 hrs, the solvent was decanted. The remaining dark red crystals were dried under vacuum. The product IndTiCl_3 was obtained.

4.5. Preparation of catalyst and cocatalyst.

1. Preparation of catalyst

IndTiCl_3 approximately 70 mg was dissolved in 50 ml. toluene under nitrogen atmosphere. The catalyst solution was shaken until the catalyst was completely soluble. The solution was used as a catalyst for styrene polymerization with methylaluminoxane cocatalyst.

2. Preparation of cocatalyst

$[\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}]$ was added in a 100 ml. glass bottle equipped with a magnetic stirrer and several fittings for nitrogen and outlet lines. Trimethylaluminum 2 M. in hexane 40 ml. were then added dropwise at 5°C for 20 hours. The solution was allowed to room temperature and stirred for 40 hours. Subsequently, the hexane solution containing methylaluminoxane was separated from hydrated-salt and used as a cocatalyst solution for ethylene polymerization with metallocene catalyst.

4.6. Styrene polymerization procedure

4.6.1. Trimethylaluminum/styrene system

4.6.1.1. Blank test

A 250 ml. glass reactor was charged with 50 ml. of toluene, and 5 ml. of styrene under nitrogen atmosphere. The glass reactor was placed in a water bath at the desired temperature and stirred for 1 hr. The reaction mixture was hydrolyzed by addition of 10% HCl in methanol, filtered, washed with excess methanol and dried 110°C .

4.6.1.2. Sample test

A 250 ml. glass reactor equipped with a mechanical stirrer was used for polymerization. Toluene 50 ml., styrene 5 ml. and various proportions of trimethylaluminum were charged to the glass reactor, in this order, under nitrogen atmosphere. The addition of trimethylaluminum was taken as the start of the polymerization reaction. The glass reactor was conducted in a water bath at the desired temperature. The polymerization reactions were stopped at intervals by addition of 10% HCl in methanol. The resulting polymer was washed with methanol several times and dried at 110°C.

The study of styrene polymerization with TMA initiator was divided into three parts.

1. The effect of polymerization time

The styrene polymerization with TMA initiator was further investigated by varying polymerization time from 10 to 120 minutes for determining the suitable time periods. The reaction temperature was 50°C. The styrene and trimethylaluminium concentrations were 1.2889 and 0.4148 mol/l. in 21.75 ml. of toluene, respectively.

2. The effect of polymerization temperature

The polymerization of styrene was further studied by varying temperature from 30°C to 70°C for 60 minutes whereas the other conditions were kept constant as section 1.

3. The effect of trimethylaluminium concentration

The polymerization of styrene was further examined by varying trimethylaluminium concentration at 50°C, the polymerization time as 120 minutes. The 0.0435 mol of styrene in toluene 21.75 ml. was required.

4.6.2. IndTiCl₃/MAO/styrene system

4.6.2.1. Blank test

A 250 ml. glass reactor equipped with a mechanical stirrer was used for polymerization. Toluene, styrene and MAO were charged to the glass reactor, in this order, under nitrogen atmosphere. The glass reactor was conducted in a water bath at the desired temperature. The polymerization reactions were terminated by addition of acidified methanol. The resulting polymer was washed with methanol several times and dried at 110°C.

4.6.2.2. Sample test

Styrene polymerization was carried out in a 250 ml. glass reactor equipped with a mechanical stirrer. Toluene 21.75 ml., various proportions of styrene, methylaluminumoxane and IndTiCl₃ catalyst was introduced to the glass reactor, in this order, under nitrogen atmosphere. The polymerization reaction was initiated by injecting the IndTiCl₃ catalyst. After polymerization for 120 minutes, the reaction mixture was quenched by adding 10% HCl in methanol. The polystyrene was immediately separated by filtration and washed with methanol several times and dried at 110°C.

The study of styrene polymerization on IndTiCl₃-methylaluminumoxane catalyst was divided into three parts.

1. The effect of IndTiCl₃ concentration

The polymerization of styrene using IndTiCl₃-methylaluminumoxane catalyst was carried out to determine the effect of IndTiCl₃ concentration. The styrene polymerization was controlled at 50°C for 120 minutes while the mole ratio of Al/Ti was 900 and 4000 for styrene/Ti in 21.75 ml. of toluene.

2. The effect of polymerization temperature

The polymerization temperature was varied from 30°C to 70°C to study the effect on the styrene polymerization. The polymerization time was 120 minutes

whereas the concentration of Ti, methylaluminoxane and styrene were 2.65×10^{-4} , 0.2386 and 1.06 M, in 21.75 ml. of toluene, respectively.

3. The effect of methylalumionoxane concentration

The styrene polymerization was further investigated by varying the methylaluminoxane concentration from Al/Ti molar ratio as 900 to 4000. The amount of IndTiCl_3 was fixed in 8.615×10^{-6} mol and styrene 0.0345 mol was required in 21.75 ml. of toluene. The polymerization reaction was kept constant at 50°C for 120 minutes.

4.7. Catalyst Characterization

4.7.1. Chemical structure

Nuclear Magnetic Resonance Spectroscopy (NMR) was used to investigate the chemical structure of catalyst. ^1H NMR spectra indicated the ratio of protons in the catalyst and showed the electronic environment of each kind of proton. ^{13}C NMR spectra illustrated carbon nucleus that each had its own electronic environment and showed the different chemical shift. The chemical shift told about the electronic environment of each hydrogen and carbon or functional groups. For the coupling constant, J , it was defined to the distance between peaks in a multiplet is a measure of the effectiveness of spin-spin coupling.

4.7.2. Active species for styrene polymerization

Electron Spin Resonance Spectroscopy (ESR) was used to investigate the active species for styrene polymerization. The values of g factor and spectrum pattern of the ESR spectrum were determined for active species, the oxidation state of metal. The measurement conditions were: microwave frequency 9.035 GHz, magnetic modulation frequency 100 kHz, central magnetic field: 3223, swift range: 100G.

4.8. Characterization of the polystyrene

Polymerization has remarkable chemical inertness to most chemicals including acids and alkalines, particularly at ordinary temperature. For this reason, there were few of chemical analysis procedure available for characterization of polystyrene. Therefore, quantitative measurements of physical properties and determinations of the involved chemicals and physical structure have become increasingly important. In this work, the polystyrene products were characterized by the following methods.

4.8.1. 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 extraction with a boiling solvent. For syndiotactic polystyrene, boiling 2-butanone was commonly used. The fraction of the whole polystyrene unextracted $\times 100$ was a percent index of syndiotacticity.

4.8.2. Microstructure Determination

Infrared spectroscopic technique is suited for the determination of microstructure of polymer such as methyl groups and unsaturation.

4.8.3. Activity

The term of catalytic activity in this work is expressed in gram of polystyrene (PS) produced by 1 mol of titanium during 1 hour of polymerization time (gPS/gTi·hr.)