

CHAPTER IV

EXPERIMENT

In the present study of 1-hexene polymerization with late transition metal catalysts, the experiment was divided into five steps.

1. Catalysts synthesis
2. Characterization of the synthesized catalysts
3. Catalyst and cocatalysts solution preparation
4. 1-Hexene polymerization with the prepared catalysts
5. Characterization of products

The details of the experiments were explained as follows.

4.1 Operation and equipments

The experiments were done in an inert atmosphere, prepurified nitrogen, using standard Schlenk technique. All equipments used in the catalyst preparation and polymerization are listed as follows :

4.1.1 Schlenk line

Schlenk line consists of nitrogen and vacuum lines. The vacuum line was equipped with the solvent trap and pump, respectively. The nitrogen line was connected to the moisture trap (purified nitrogen gas by passing through molecular sieve, NaOH and P₂O₅, respectively) and the oil bubbler that contained enough oil to provide a seal from the atmosphere. The Schlenk line was shown in Figure 4.1.

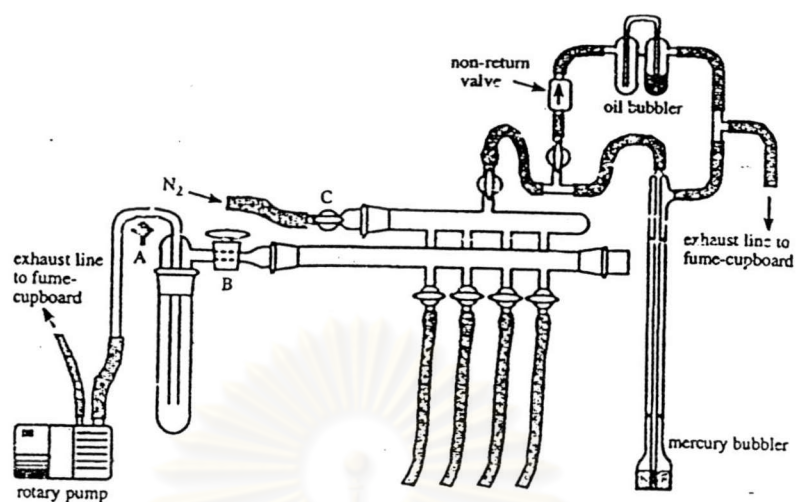


Figure 4.1 Schlenk line.

4.1.2 Schlenk flask

A flask with a side-arm is used with inert gas. It has a side-arm to connect to the Schlenk line manifold. Some typical models are shown in Figure 4.2.

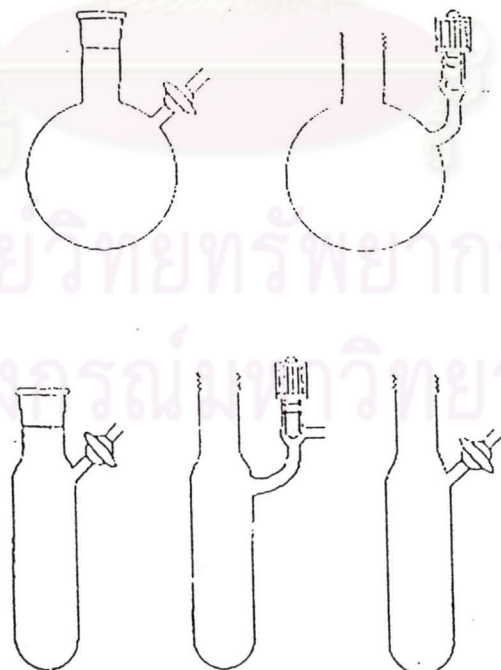


Figure 4.2 Round-bottomed, Schlenk flasks and Schlenk tubes.

4.1.3 Vacuum pump

A pressure of $10^{-3} - 10^{-1}$ mm Hg generated from EDWARDS Provac high vacuum pump model RV 8 England was adequate for the vacuum supply to the vacuum line in the Schlenk line.

4.1.4 Heating bath

The silicone oil heating bath with thermometer was used to hold the temperature of polymerization reaction.

4.1.5 Inert gas supply

Ultra high purity nitrogen gas was purified by passing through three columns packed with molecular sieve 4⁰A, NaOH and P₂O₅, respectively. The inert gas was used to feed in the nitrogen line of the Schlenk line and polymerization reactor.

4.1.6 Syringe and needle

The Top syringes Japan with volume of 50, 10, 5, 2, 1 and 0.5 mL. Needles No. 19, 20, and 22 were used.

4.1.7 Glove bag

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

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4.2 Chemicals

The chemicals used in this experiment are analytical grade, except critical materials are specified as follows:

Table 4. Chemical reagents and suppliers

Chemicals	Suppliers
1. Ultra high purity nitrogen gas (99.999%)	Thai Industry Gas Co.,Ltd., Thailand
2. Toluene	Lab Scans Co., Ltd., Ireland
3. Tetrahydrofuran	Lab Scans Co., Ltd., Ireland
4. Dichloromethane	Merck, Germany
5. Ethanol	Merck, Germany
6. Diethyl ether	Lab Scans Co., Ltd., Ireland
7. 2,6-Diisopropylaniline	Aldrich Chemical Company.
8. Butyl lithium(n-BuLi)	Merck, Germany
9. Tetramethylethylenediamine(tmeda)	Merck, Germany
10.1,3-Dibromopropane	Fluka Chemie A.G., Switzerland
11. Acetylacetone	Fluka Chemie A.G., Switzerland
12. Ferric chloride anhydrous (FeCl ₃)	Fluka Chemie A.G., Switzerland
13. 1-Hexene	Fluka Chemie A.G., Switzerland
14. Ethylene bis(indenyl)zirconium dichloride, Et(Ind) ₂ ZrCl ₂	Aldrich Chemical Company, Inc., USA
15. Dimethylanilinium tetrakis(pentafluoro- phenyl)borate, [PhNMe ₂ H][B(C ₆ F ₅) ₄]	Donated from DOW Chemical Company, USA
16. Methyl magnesium bromide (MeMgBr) 1.0 M in diethyl ether	Aldrich Chemical Company, Inc., USA
17. Tri-isobutylaluminium (TIBA)	Donated from Japan Advanced Institute of Science and Technology (JAIST), Japan
18. Silica gel	Merck, Germany
19. 8-Quinolinol	Fluka Chemie A.G., Switzerland

In this work, several reagents react violently with water and ignite spontaneously in air (by reaction with oxygen and/or moisture). So they were handled safely using inert atmosphere techniques (Schlenk and glove bag techniques). Also, the chemicals and solvents were dried before use with following methods:

1. Non - halogenated solvent was purified by refluxing over sodium / benzophenone and distilled under nitrogen atmosphere.
3. Dichloromethane, acetonitrile and hexane were purified by refluxing with calcium hydride before use.
4. Diethyl ether and ethanol were dried by adding molecular sieves into the solvent.
5. 1-Hexene was dried over calcium hydride and distilled before use.
6. Methylaluminoxane (MAO) cocatalyst has 9%w/v Al.

In low temperature reactions, the mixture of dry ice and acetone (1:1) was used to control the temperature at -78°C . The mixture of dry ice and acetonitrile was used for temperature of -45°C . The temperature of -20°C was obtained by mixing dry ice with carbon tetrachloride.

4.3 Characterization methods

The methods used to characterize catalyst and polymer products are specified in the following:

4.3.1 Fourier transform infrared spectrometry (FT-IR)

Fourier transform infrared spectra of the polymers and complexes were recorded on Nicolet FT-IR Impact 410 Spectrophotometer at Department of Chemistry, Chulalongkorn University. The liquid samples were coated on NaCl cells. The solid samples were prepared by pressing the sample with KBr. Infrared spectra were recorded between 400 cm^{-1} to $4,000\text{ cm}^{-1}$ in transmittance mode.

4.3.2 Nuclear magnetic resonance spectroscopy (NMR)

^1H -NMR and ^{13}C -NMR spectra were obtained on Bruker ACF 200 MHz at Department of Chemistry, Chulalongkorn University. The NMR spectra were measured in chloroform-d at room temperature. Broad-band decoupling was used to remove the ^{13}C - ^1H coupling. The center peak of chloroform-d was used as the internal reference (^1H -NMR at 7.2 ppm and ^{13}C -NMR at 77.0 ppm).

4.3.3 Differential scanning calorimetry (DSC)

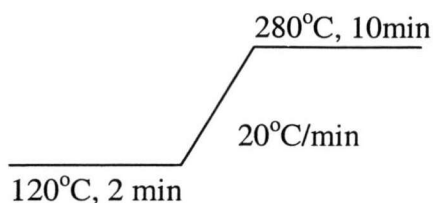
The melting temperature (T_m) and the glass transition temperature (T_g) of the polymers were determined by a NETZSCH DSC 200 at the Scientific and Technological Research Equipment Center (STREC), Chulalongkorn University. The analyses were performed at the heating rate of $10^\circ\text{C}/\text{min}$.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

4.3.4 Gel permeation chromatography (GPC)

GPC curves of polymers were determined on a Waters 150-CV GPC at the National Metal and Materials Technology Center (MTEC), the National Science and Technology Development Agency (NSTDA). The molecular weight and molecular weight distribution of the polymer was measured at room temperature using THF as an eluent solvent at a flow rate of $1\text{ mL}/\text{min}$ by Waters 150-C column (column TL gel $10\ \mu\text{m}$ mixed B 2 column, Reflective Index detector and injection volumn $100\ \mu\text{L}$). Polystyrene standards molecular weight in range 500 to 1,000,000 were used for calibration.

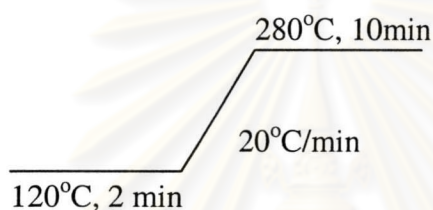
4.3.5 Gas chromatography – mass spectrometry (GC-MS)

Gas chromatography was carried out on Varian, Star 3400 CX and mass spectrometry was carried out on Varian, Saturn 4D at Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University.



4.3.6 Gas chromatography (GC)

Gas chromatography was carried out on Shimadzu GC-14B gas chromatograph that equipped with 30-m long and 0.25-mm inner diameter DB-1 (0.25 μm film thickness) column, Chulalongkorn University.



4.3.7 Ultraviolet and visible spectrophotometry

UV-visible spectra were recorded on JENWAY spectronic. Wavelength is in range of 200-800 nm and cell width is 1 cm.

4.3.8 Melting point

Melting point of complexes were measured in glass capillaries using electrothermal apparatus. The uncorrected melting points were reported in degree Celsius.

4.3.9 Elemental analyses

Elemental analyses of **cpx 1a** and **cpx 3c** were carried out on Perkin Elmer Elemental Analyser 2400 CHN, by ignition combustion gas chromatography separated by frontal analysis and quantitatively detected by thermal conductivity detector. This technique was performed at Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University. Elemental analyse of **cpx 2b** was carried out on CHNS analyzer Perkin Elmer TE 2400 series II USA at Department of Chemistry, Faculty of Science, Chiangmai University.

4.3.10 Atomic absorption spectroscopy

Atomic absorption spectroscopy was used for determining the amount of iron. This technique was performed by Scientific and Technological Research Equipment Centre (STREC), Chulalongkorn University.

4.4 Procedures for catalysts synthesis

4.4.1 Ligand synthesis

4.4.1.1 Synthesis of 1,3-di(2,6-diisopropylphenyl)aminopropane ; RHN (CH₂)₃NHR (R = 2,6-ⁱPr₂C₆H₃), ligand (**a**)

Into a 100-mL two-necked round bottom flask equipped with a magnetic bar, BuLi 35.00 mL (15% in hexane, 57.00 mmol) was added dropwise to a stirring solution of 2,6-diisopropylaniline 9.50 mL (50.00 mmol) in THF 37 mL at -78°C. The solution was warmed to room temperature where it was kept for 30 minutes. The solution was cooled to 0°C and tmeda 7.50 mL (50.00 mmol) was added dropwise followed by 1,3-dibromopropane 2.50 mL (25.00 mmol), then stirred overnight at room temperature. The solution was poured into water 30 mL and extracted with dichloromethane (3x15 mL). The organic layer was dried over anhydrous Na₂SO₄ and the dichloromethane was removed by using rotary evaporator. The resulting orange oil was purified by silica gel column chromatography using dichloromethane : hexane (7:3) as eluent. The first eluted fraction as orange oil (8.69 g, 88 %yield) was obtained after removing the solvent.

¹H-NMR(CDCl₃): δ (ppm) 7.12 (m, 6H), 3.37 (sept, 4H), 3.02 (t, 4H), 2.97 (t, 2H), 1.77 (t, 2H), 1.26 (d, 24H)

ref.^[50] (300 MHz, C₆D₆) : δ (ppm) 7.10 (m, 6H), 3.36 (sept, 4H), 3.01 (t, 4H), 2.97 (s, 2H), 1.77 (pent, 2H), 1.22 (d, 24H)

¹³C-NMR(CDCl₃): δ (ppm) 143.5, 142.4, 123.6, 50.3, 32.4, 27.8, 24.4

ref.^[50] (300 MHz, C₆D₆) : δ = 144.0, 143.7, 123.9, 50.8, 32.7, 28.1, 24.5

FT-IR (NaCl): ν (cm⁻¹) 3371(w), 3050(w), 2950(s), 2865(s), 1621(w), 1451 (s), 1362(m), 1254(m), 1103(m), 798(m), 753(s)

UV-Visible Spectrum: $\lambda_{\max} = 279 \text{ nm}$, $\epsilon = 13,587$

4.4.1.2 Synthesis of 1-((2,6-diisopropylphenyl)amino)-4-((2,6-diisopropylphenyl)imino)-2-pentene ; $\text{RHN}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{C}=\text{NR}$
($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$), ligand (**b**)

Into a 250-mL three-necked round bottom flask equipped with a magnetic bar and a reflux condenser, concentrated hydrochloric acid 0.04 mL (4.80 mmol) was added to a solution of 2,4 - pentanedione 0.50 mL (4.90 mmol) and 2,6 - diisopropylaniline 2.08 mL (11.00 mmol) in ethanol 20 mL. The reaction mixture was heated at reflux for 3 days and concentrated to a brown residue. The crude product was extracted with 10 mL of dichloromethane. After stirring with 20 mL solution of saturated K_2CO_3 , the organic layer was separated. Evaporation of solvent and recrystallization from methanol afforded the compound as a white crystalline solid (0.95 g, 46 %yield).

Melting point 140-141°C

$^1\text{H-NMR}(\text{CDCl}_3)$: δ (ppm) 12.09 (br, 1H), 7.10 (m, 6H), 4.84 (s, 1H), 3.09 (m, 4H), 1.69 (s, 6H), 1.20 (d, 12H), 1.12 (d, 12H)

ref.^[12] (CDCl_3) : δ (ppm) 12.12 (br, 1H), 7.12 (m, 6H), 4.84 (s, 1H), 3.10 (m, 4H), 1.72 (s, 6H), 1.22 (d, 12H), 1.12 (d, 12H)

FT-IR (KBr): ν (cm^{-1}) 3381(w), 2959(s), 2880(w), 1625(s), 1550(s), 1442 (m), 1376(w), 1277(m), 753(w)

UV-Visible Spectrum: $\lambda_{\max} = 320 \text{ nm}$, $\epsilon = 32,000$

4.4.1.3 Synthesis of bis(salicylaldehyde)*N,N'*-ethylenediimine (salen), ligand (c)

Into a 100-mL two-necked round bottom flask equipped with a magnetic bar, ethylenediamine 5.00 mL (60.00 mmol) was slowly added to salicylaldehyde 18.30 mL (150.00 mmol) and stirred at room temperature. The yellow precipitate occurred immediately and was recrystallized from 95% ethanol. Bright yellow crystals (15.67 g, 97 %yield) were obtained.

Melting point 124-125°C

¹H-NMR(CDCl₃): δ (ppm) 8.34 (s, 2H), 7.29 (dt, 2H), 7.21 (dd, 2H), 6.92 (d, 2H), 6.83 (dt, 2H), 3.93 (s, 4H)

ref.^[62] (200 MHz, CDCl₃) : δ (ppm) 13.2 (s, 2H) , 8.29 (s, 2H), 7.26 (dt, 2H), 7.18 (dd, 2H), 6.93 (d, 2H), 6.83 (dt, 2H), 3.84 (s, 4H)

FT-IR (KBr): ν (cm⁻¹) 3430(w), 3054 (w), 2900(w), 1635(s), 1573(s), 1496 (s), 1280(s), 1149(s), 856 (s), 748(s)

ref.^[62] : 3500(w), 3010-3050(w), 2870-2950(w), 1750-2000(w), 1640(s), 1450-1600(s), 1280(s) and 1170(s)

UV-Visible Spectrum: λ_{max} = 258 nm, ε = 50,930 and λ_{max} = 318 nm, ε = 20,930

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4.4.2 Synthesis of iron complexes

4.4.2.1 Synthesis of $[\text{RHN}(\text{CH}_2)_3\text{NHR}]\text{FeCl}_3$ ($\text{R} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$) complex, **cpx 1a**

Into a 100-mL two-necked round bottom flask equipped with a magnetic bar and a reflux condenser, a solution of $\text{RHN}(\text{CH}_2)_3\text{NHR}$ ($\text{R} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$) ligand (**a**) 3.60 g (14.24 mmol) in 25 mL acetonitrile was added anhydrous FeCl_3 2.23 g (13.70 mmol). The mixture was refluxed for 4 hr to obtain dark red solution with red powder. The red powder was separated by filtration through frit. The dark red filtrate was pumped off solvent and added diethyl ether to precipitate the dark red solids (2.75 g, 36 %yield).

FT-IR (KBr): ν (cm^{-1}) 3409(w), 2968(s), 1574(s), 1461(s), 1367(w), 1051(w), 805(w)

Elemental analysis: Calc; %C, 58.23; %H, 7.60; %N, 5.03; %Fe, 10.04

Found; %C, 58.19; %H, 8.26; %N, 5.06; %Fe, 9.70

Molecular formula: $\text{C}_{27}\text{H}_{42}\text{N}_2\text{FeCl}_3$

Molucular weight: 556.35

UV-Visible Spectrum: $\lambda_{\text{max}} = 491$ nm, $\epsilon = 221$ and $\lambda_{\text{max}} = 551$ nm, $\epsilon = 219$

4.4.2.2 Synthesis of $[\text{RHN}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{C}=\text{NR}]\text{FeCl}_3$ ($\text{R} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$) complex, **cpx 2b**

Into a 100-mL two-necked round bottom flask equipped with a magnetic bar and a reflux condenser, anhydrous FeCl_3 0.12 g (0.73 mmol) was added to a solution of $\text{RHN}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{C}=\text{NR}$ ($\text{R} = 2,6\text{-}^i\text{PrC}_6\text{H}_3$) ligand (**b**) 0.28 g (0.66 mmol) in 20 mL dichloromethane. The mixture was refluxed for 4 hr and stirred at room temperature overnight. The crude red solid was obtained after pumping off

solvent. Chloroform 10 mL was added to dissolve the solid. After filtration, yellow filtrate was evaporated off solvent to obtain orange precipitates (0.0985 g, 26 %yield).

FT-IR (KBr): ν (cm^{-1}) 3428(w), 2970(m), 2809(m), 1503(s), 1428(m), 1296 (s), 1103(s), 1037(s), 798(s)

Elemental analysis: Calc; %C, 54.11; %H, 6.61; %N, 4.21; %Fe, 8.39

Found; %C, 54.27; %H, 6.37; %N, 4.40; %Fe, 8.70

Molecular formula: $\text{C}_{29}\text{H}_{42}\text{N}_2\text{FeCl}_3 \cdot \text{CH}_2\text{Cl}_2$

Molecular weight: 665.35

UV-Visible Spectrum: $\lambda_{\text{max}} = 466$ nm, $\epsilon = 3691$ and $\lambda_{\text{max}} = 626$ nm, $\epsilon = 1047$

4.4.2.3 Synthesis of Fe(III)Salen complex, **cpx 3c**

Into a 100-mL two-necked round bottom flask equipped with magnetic bar, bis(salicylaldehyde)N,N'-ethylenediimine (salen) 0.27 g (1.00 mmol) was dissolved in ethanol at 70°C. After stirring the solution until homogeneity, FeCl_3 0.16 g (1.00 mmol) dissolved in ethanol was dropped slowly and refluxed for 1 hr. Precipitate had occurred. It was filtered, washed with cold ethanol and recrystallized from ethanol:dichloromethane (50:50) to give dark purple crystal (0.1552 g, 43 %yield).

FT-IR (KBr): ν (cm^{-1}) 3054(w), 2900 (w), 1627(s), 1442 (s), 1303(s), 1126 (w), 902(s), 755(s)

Elemental analysis: Calc; %C, 53.73; %H, 3.92; %N, 7.83

Found; %C, 53.78; %H, 3.35; %N, 7.57

Molecular formula: $\text{C}_{16}\text{H}_{14}\text{N}_2\text{O}_2\text{FeCl}$

Molecular weight: 357.35

UV-Visible Spectrum: $\lambda_{\text{max}} = 475$ nm, $\epsilon = 8,403$

4.5 Preparation of catalyst and cocatalyst solution

4.5.1 $[\text{RNH}(\text{CH}_2)_3\text{NHR}]\text{FeCl}_3$ ($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) (**cpx 1a**) catalyst stock solution (1.0×10^{-3} M)

$[\text{RNH}(\text{CH}_2)_3\text{NHR}]\text{FeCl}_3$, red solid 0.0278 g (50.0×10^{-6} mol) was dissolved in 50.00 mL distilled dichloromethane in a Schlenk flask.

4.5.2 $[\text{RHN}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{C}=\text{NR}]\text{FeCl}_3$ ($\text{R} = 2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$) (**cpx 2b**) catalyst stock solution (1.0×10^{-3} M)

$[\text{RHN}(\text{CH}_3)\text{C}=\text{C}(\text{CH}_3)\text{C}=\text{NR}]\text{FeCl}_3$, orange solid 0.0294 g (50.0×10^{-6} mol) was dissolved in 50.00 mL distilled dichloromethane in a Schlenk flask.

4.5.3 Fe(III)salen (**cpx 3c**) catalyst stock solution (1.5×10^{-3} M)

Fe(III)salen, dark purple crystal 0.0269 g (7.5×10^{-5} mol) was dissolved in 50.00 mL distilled dichloromethane in a Schlenk flask with a magnetic bar. The solution was stirred under nitrogen atmosphere until all of the solid dissolved.

4.5.4 *rac*-Et bis(Ind)₂ZrCl₂ catalyst stock solution (3.3×10^{-3} M)

rac-Et bis(Ind)₂ZrCl₂, yellow-brownish solid 0.0836 g (2.0×10^{-4} mol) was dissolved in 60.00 mL distilled toluene in a Schlenk flask.

4.5.5 $[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ cocatalyst stock solution (5.0×10^{-3} M)

$[\text{PhNMe}_2\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$, white solid, 0.2000 g (2.5×10^{-4} mol) was dissolved in 50.00 mL distilled toluene in a Schlenk flask.

4.5.6 $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ cocatalyst stock solution (1.72×10^{-3} M)

$[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$, orange solid, 0.0793 g (8.6×10^{-5} mol) was dissolved in 50.00 mL distilled toluene in a Schlenk flask.

4.5.7 Triisobutylaluminum (TIBA) stock solution (0.05 M)

1.25 mL of TIBA solution (2.00 M) was mixed with 98.75 mL of distilled toluene to get 0.05 M.

4.6 Polymerization procedure

Polymerization of 1-hexene was carried out under dry nitrogen atmosphere in a 100 ml round bottomed Schlenk flask with a magnetic bar.

1. Using boron cocatalyst

A catalyst solution was firstly alkylated by mixing with TIBA or MeMgBr or PhMgCl. The mixture was stirred at room temperature for 1 hr. After that, a boron cocatalyst solution was added and stirred for 1 hr. After the reaction mixture was equilibrated to the desired temperature and stirred for 30 minutes, 1-hexene monomer was injected to start the polymerization. Finally, the polymerization was terminated by adding 5% aqueous hydrochloric acid. The mixture was extracted with chloroform. The organic layer was separated and dried over Na₂SO₄. The product was obtained after evaporation of the solvent.

2. Using MAO cocatalyst

MAO was mixed with a solution of catalyst and stirred at room temperature for 1 hr, then equilibrate to the desired temperature for 30 minutes. The next steps were the same as in 1.

4.7 Catalyst activity

Activity in this experiment can be calculated by the equation

$$\text{Activity} = (\text{kilograms of polymer}) / (\text{mole of catalyst})$$

4.8 % Yield

% Yield in this experiment can be calculated by the equation

$$\% \text{ Yield} = \frac{\text{grams of product (obtained)} \times 100}{\text{grams of product (theory)}}$$