

## CHAPTER III EXPERIMENTAL

### 3.1 Ethylene Copolymerization by Half-Titanocenes Containing Imidazolin-2-Iminato Ligands – MAO Catalyst System

#### 3.1.1 General Procedures

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and were used without further purification. Anhydrous grade 1-hexene and 1-dodecene (Kanto Chemical Co., Inc.) were stored in bottles in the drybox in the presence of molecular sieves and were passed through an alumina short column before use. Toluene and AlMe<sub>3</sub> in the commercially available methylaluminoxane [PMAO-S. 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, AlMe<sub>3</sub> and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Cp'TiCl<sub>2</sub>[1,3-R<sub>2</sub>(CHN)<sub>2</sub>C=N] [Cp' = Cp (1), 'BuC<sub>5</sub>H<sub>4</sub> (2); R = 'Bu (1,3-di-*tert*-butylimidazolin-2-imide, **a**), 2,6-'Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub> (1,3-diisopropylphenyl imidazolin-2-imide, **b**)] were prepared according to previous reports (Tamm *et al.*, 2004 and 2006)]. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received.

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for <sup>1</sup>H, 125.77 MHz for <sup>13</sup>C) and all chemical shifts are given in ppm and are referenced to SiMe<sub>4</sub>. Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from <10<sup>2</sup> to <2.8×10<sup>8</sup> MW) at 140 °C using *o*-

dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

### 3.1.2 Ethylene polymerization

Ethylene polymerizations were conducted in toluene by using a 100 mL scale autoclave. Toluene (29.0 mL) and prescribed amount of MAO white solid were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of complex via a syringe, the reaction apparatus was pressurized to 5 atm (total 6 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo*.

### 3.1.3 Copolymerization of ethylene with 1-hexene, 1-dodecene

Experimental procedures for the copolymerization of ethylene with 1-hexene, 1-decene were the same as those for the ethylene polymerization described above except that prescribed amount of 1-hexene or 1-decene was added into an autoclave and the total volume was set to 30 mL.

## **3.2 Efficient Ethylene/Norbornene Copolymerization by Half-titanocenec Containing Imidazoli-2-Iminato ligands – MAO catalyst system**

### 3.2.1 General Procedures

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and was used without further purification. Norbornene of

reagent grade (TCI Co., Ltd.) stored in the drybox was used as received.  $\text{Cp}'\text{TiCl}_2[1,3\text{-R}_2(\text{CHN})_2\text{C}=\text{N}]$  [ $\text{Cp}' = \text{Cp}$  (1),  $\text{'BuC}_3\text{H}_4$  (2);  $\text{R} = \text{'Bu}$  (a), 2,6- $\text{'Pr}_2\text{C}_6\text{H}_3$  (b)] were prepared according to previous reports (Tamm *et al.*, 2004 and 2006). Toluene and  $\text{AlMe}_3$  in the commercially available methylaluminoxane [PMAO-S. 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene,  $\text{AlMe}_3$  and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received.

All  $^{13}\text{C}$  NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for  $^1\text{H}$ , 125.77 MHz for  $^{13}\text{C}$ ) and all chemical shifts are given in ppm and are referenced to  $\text{SiMe}_4$ . Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT  $\times$  2, 30 cm  $\times$  7.8 mm i.d.), ranging from  $<10^2$  to  $<2.8 \times 10^8$  MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

### 3.2.2 Copolymerization of ethylene with norbornene (NBE)

Ethylene copolymerizations were conducted in toluene by using a 100 mL scale autoclave. Toluene (29.0 mL), prescribed amount of MAO white solid, and norbornene were charged into the autoclave in the drybox, and the apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of complex via a syringe, the reaction apparatus was pressurized to 5 atm (total 6 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo*.

### 3.3 Facile Efficient Terpolymerization of Ethylene, Styrene with $\alpha$ -Olefins by Aryloxo Modified Half-Titanocenes - Cocatalyst System

#### 3.3.1 General Procedures

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and was used without further purification. Anhydrous grade 1-hexene and 1-decene (Kanto Chemical Co., Inc.) were stored in bottles in the drybox in the presence of molecular sieves and were passed through an alumina short column before use. Reagent grade of styrene (Kanto Chemical Co., Inc.) and *p*-methylstyrene (TCI Co., Ltd.) were stored in a freezer after passing through an alumina short column under nitrogen flow in the drybox. Al<sup>t</sup>Bu<sub>3</sub> was purchased from Kanto Chemical Co., Inc., and [PhN(H)Me<sub>2</sub>][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] was purchased from Asahi Glass Co., Ltd. Toluene and AlMe<sub>3</sub> in the commercially available methylaluminoxane [PMAO-S. 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene, AlMe<sub>3</sub> and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Cp\*TiCl<sub>2</sub>(O-2,6-<sup>t</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1) and (<sup>t</sup>BuC<sub>5</sub>H<sub>4</sub>)TiCl<sub>2</sub>(O-2,6-<sup>t</sup>Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (2) were prepared according to previous reports (Nomura *et al.*, 1998). Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received.

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz, <sup>1</sup>H; 125.77 MHz, <sup>13</sup>C) and all chemical shifts are given in ppm and are referred to SiMe<sub>4</sub>. <sup>13</sup>C NMR spectra for the resultant polymers were recorded with proton decoupling, and the pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients accumulated was ca. 6000. The copolymer samples for analysis were prepared by dissolving the

polymers in 1,1,2,2-tetrachloroethane- $d_2$  solution, and the spectra was measured at 110 °C.

Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT  $\times$  2, 30 cm  $\times$  7.8 mm i.d.), ranging from  $<10^2$  to  $<2.8 \times 10^8$  MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

### 3.3.2 Terpolymerization of ethylene with 1-hexene (1-decene) and styrene (*p*-methylstyrene)

Ethylene terpolymerizations were conducted in toluene by using a 100 mL scale autoclave. Typical procedure is as follows. A prescribed amount of MAO white solid, prepared by removing toluene and  $\text{AlMe}_3$  from commercially available MAO (PMAO-S, Tosoh Finechem Co.), 1-hexene (or 1-decene) and styrene were charged into the autoclave in the drybox, and the total volume of toluene and comonomer was set to 29.0 mL. The apparatus was placed under ethylene atmosphere (1 atm). After an addition of a toluene solution (1.0 mL) containing a prescribed amount of complex via a syringe, the reaction apparatus was pressurized to 5 atm (total 6 atm), and the mixture was stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo*.

The terpolymerizations in the presence of  $\text{Al}^i\text{Bu}_3$  and  $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$  were carried out under the same conditions described above except that  $\text{Al}^i\text{Bu}_3$  was charged in place of MAO: a prescribed amount of toluene solution (1.0 mL) containing titanium catalyst was then added, immediately followed by addition of a toluene solution (1.0 mL) containing  $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ . The copolymerization with *p*-methylstyrene was conducted under the same conditions described above except that *p*-methylstyrene was used in place of styrene.

According to the previous report (Nomura *et al.*, 2000-2005), the resultant polymer mixture was separated into two fractions, and atactic polystyrene prepared only by MAO itself was extracted with acetone; copolymer prepared by titanium complexes - MAO catalyst was isolated as the acetone insoluble fraction. The basic procedure is as follows. The polymer sample obtained in the polymerization experiment was added into a round bottom flask containing acetone equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate acetone soluble and insoluble fraction. Then the acetone insoluble fraction was dried *in vacuo*. The microstructure analyses in the resultant copolymers were estimated by the  $^{13}\text{C}$  NMR spectra of the copolymer, and each of the resonances were assigned by comparison with the previous reports (Nomura *et al.*, 2000 and 2002). The styrene contents were estimated based on ratio of the total integration values of styrene vs ethylene at each resonances in the  $^1\text{H}$  NMR spectra (Nomura *et al.*, 2012).

### **3.4 Facile Efficient Introduction of Reactive Functionality by Terpolymerization of Ethylene, Styrene or 1-Hexene with Divinyl Biphenyl by Aryloxo Modified Half-Titanocenes - Cocatalyst System**

#### **3.4.1 General Procedures**

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. All chemicals used were of reagent grade and were purified by the standard purification procedures. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3 Å 1/16 and 4 Å 1/8, and 13X 1/16) under a nitrogen stream in the drybox and was used without further purification. Anhydrous grade 1-hexene was stored in bottles in the drybox in the presence of molecular sieves and was passed through an alumina short column before use. Reagent grade of styrene (Kanto Chemical Co., Inc.) was stored in a freezer after passing through an alumina short column under nitrogen flow in the drybox. 3,3-Divinylbiphenyl was received from Nippon Steel & Sumikin Chemical Co., Ltd., and was passed through an alumina short column before use. Toluene and  $\text{AlMe}_3$  in the commercially available methylaluminoxane [PMAO-S. 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.]

were removed under reduced pressure (at ca. 50 °C for removing toluene, AlMe<sub>3</sub> and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Cp\*TiCl<sub>2</sub>(O-2,6-'Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (1) (Nomura *et al.*, 1998), ('BuC<sub>5</sub>H<sub>4</sub>)TiCl<sub>2</sub>(O-2,6-'Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (2) (Nomura *et al.*, 1998), and (1,2,4-Me<sub>3</sub>C<sub>5</sub>H<sub>2</sub>)TiCl<sub>2</sub>(O-2,6-'Pr<sub>2</sub>C<sub>6</sub>H<sub>3</sub>) (3) (Nomura *et al.*, 2000) were prepared according to previous reports. *n*-BuLi was purchased from Kanto Chemical Co., Inc. Ethylene for polymerization was of polymerization grade (purity >99.9%, Sumitomo Seika Co., Ltd.) and was used as received.

All <sup>1</sup>H and <sup>13</sup>C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for <sup>1</sup>H, 125.77 MHz for <sup>13</sup>C) and all chemical shifts are given in ppm and are referred to SiMe<sub>4</sub>. <sup>13</sup>C NMR spectra for the resultant polymers were recorded with proton decoupling, and the pulse interval was 5.2 s, the acquisition time was 0.8 s., the pulse angle was 90°, and the number of transients accumulated was ca. 6000. The copolymer samples for analysis were prepared by dissolving the polymers in 1,1,2,2-tetrachloroethane-*d*<sub>2</sub> solution, and the spectra was measured at 110 °C. Molecular weights and molecular weight distributions for the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with a polystyrene gel column (TSK gel GMHHR-H HT × 2, 30 cm × 7.8 mm i.d.), ranging from <10<sup>2</sup> to <2.8×10<sup>8</sup> MW) at 140 °C using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples..

#### 3.4.2 Terpolymerization of ethylene and styrene with 3,3'-divinylbiphenyl.

The ethylene copolymerizations were conducted in toluene by using a 100 mL scale autoclave. A prescribed amount of MAO white solid, prepared by removing toluene and AlMe<sub>3</sub> from commercially available MAO (PMAO-S, Tosoh Finechem Co.), styrene and 3,3-divinylbiphenyl were charged into the autoclave in the drybox, and the total volume of toluene and comonomer was set to 29 mL. The apparatus was placed under ethylene atmosphere (1 atm). After the addition of a toluene solution (1.0 mL) containing a prescribed amount of complex via a syringe, the reaction apparatus was pressurized to 5 atm (total 6 atm), and the mixture was

stirred magnetically for 10 min. After the above procedure, ethylene was purged, and the mixture was then poured into MeOH (150 mL) containing HCl (10 mL). The resultant polymer was collected on a filter paper by filtration and was adequately washed with MeOH and then dried *in vacuo*. According to the previous report (Nomura *et al.*, 1998), the resultant polymer mixture was separated into two fractions, and atactic polystyrene prepared only by MAO itself was extracted with acetone; copolymer prepared by titanium complexes - MAO catalyst was isolated as the acetone insoluble fraction. Terpolymerizations of ethylene and 1-hexene with DVBP were conducted similarly, except that 1-hexene was used in place of styrene.

#### 3.4.3 Post-polymerization of poly(ethylene-co-styrene-co-3,3-divinyl biphenyl) with styrene initiated by *n*-BuLi.

The prepared poly(ethylene-co-styrene-co-3,3'-divinyl-biphenyl) sample (40 mg, run 5) was dissolved in toluene (10 mL) and was cooled to -30 °C. After an addition of toluene solution (1 mL) containing *n*-BuLi (16.0 μmol, 0.4 equiv to the vinyl group), the reaction mixture was stirred for 90 min at room temperature. Styrene (30 mL) was then added and the mixture was stirred at 50 °C for 3 h. After the above procedure, the mixture was poured into methanol. The resultant polymer was collected by filtration and was then dried *in vacuo* at 60 °C. Atactic polystyrene was extracted with acetone (trace amount, 1.2 mg); the grafted polymer was isolated as the acetone insoluble fraction. Yield 47.0 mg.  $M_n = 8.67 \times 10^4$ ,  $M_w/M_n = 2.42$ , styrene content (in the whole polymer) 50.6 mol% estimated by the <sup>1</sup>H NMR spectrum.