CHAPTER III

EXPERIMENTAL

In the present study of the copolymerization of ethylene/α-olefin with the various MCM-41 supported zirconocene catalysts, the experiments were divided into four parts:

(i)   Preparation of various MCM-41 supports

(ii)   Preparation of various MCM-41 supported dried MMAO

(iii)   Ethylene and /α-olefin copolymerization procedure

(iv)   Characterization of ethylene and α-olefin copolymer products, supports and catalyst precursor MCM-41 supported dried MMAO

The details of the experiments are explained as follows.

3.1 Chemicals

The chemicals used in these experiments were analytical grade, but only major materials are specified as follows:

1. Ludox HS-40 colloidal silica, 40 wt% suspension in water was purchased from Sigma-Aldrich Company,Inc. and use as received.

2. Cetyltrimethylammonium bromide was purchased from Aldrich Chemical Company,Inc. and use as received.

3. N,N-Dimethyldecylamine was purchased from Aldrich Chemical Company, Inc. and use as received.

4. Sodium hydroxide was purchased from Merck KGaA. and use as received

5. Ammonia solution 25% was purchased from Merck KGaA. And use as received.

6. Acetic acid was purchased from Merck KGaA. and use as received.

7. rac-Ethylenebis(indenyl)zirconium dichloride (Et(Ind)$_2$ZrCl$_2$) was supplied from Aldrich Chemical Company, Inc. and used without further purification.

8. Ethylene gas (99.96%) was devoted from National Petrochemical Co., Ltd., Thailand and used as received.

9. 1-Hexene (99+%) was purchased from Aldrich Chemical Company, Inc. and purified by distilling over sodium under argon atmosphere before use.

10. 1-Octene (98%) was purchased from Aldrich Chemical Company, Inc. and used as received.

11. 1-Decene (≥ 97%) was purchased from Fluka Chemie A.G. Switzerland. and used as received.

12. Modified Methylaluminoxane (MMAO) 5.6% wt inhexane was donated from Tosoh Akso, Japan and used without further purification.

13. Trimethylaluminum [Al(CH$_3$)$_3$] 2.0 M in toluene was supplied from Nippon Aluminum Alkyls Ltd., Japan and used without further purification.

14. Hydrochloric acid (Fuming 36.7%) was supplied from Sigma.

15. Ethylene gas (polymerization grade) was devoted from National Petrochemical Co., Ltd., Thailand.

16. Methanol (Commercial grade) was purchased from SR lab.

17. Toluene was devoted from EXXON Chemical Ltd., Thailand. This solvent was dried over dehydrated CaCl$_2$ and distilled over sodium/benzophenone under argon atmosphere before use.

18. Ultra high purity argon gas (99.999%) was purchased from Thai Industrial Gas Co., Ltd., and further purified by passing through columns packed with molecular sieve 3 A, BASF Catalyst R3-11G, sodium hydroxide (NaOH) and phosphorus pentaoxide (P$_2$O$_5$) to remove traces of oxygen and moisture.

3.2 Equipments

All types of equipments used in the catalyst precursor preparation and polymerization are listed below:

3.2.1 Cooling system

The cooling system was in the solvent distillation in order to condense the freshly evaporated solvent.

3.2.2 Inert gas supply

The inert gas (argon) was passed through columns of BASF catalyst R3-11G as oxygen scavenger, molecular sieve 3×10^{-10} m to remove moisture. The BASF catalyst was regenerated by treatment with hydrogen at 300 °C overnight before flowing

the argon gas through all the above columns. The inert gas supply system is shown in Figure 3.1.
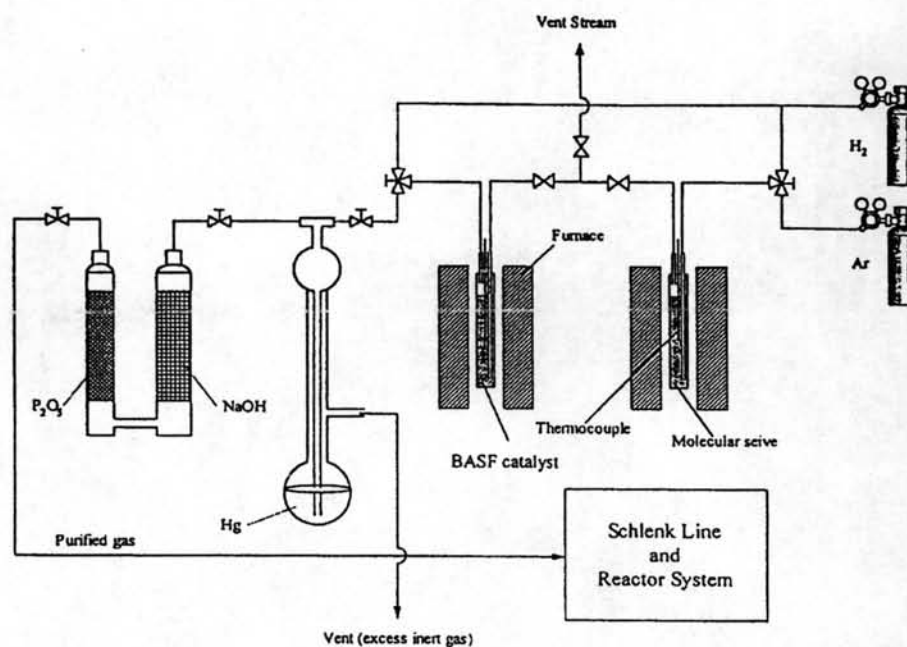

Figure 3.1 Inert gas supply system

3.2.3 Magnetic stirrer and heater

The magnetic stirrer and heater model RTC basis from IKA Labortechnik were used.

3.2.4 Reactor

A 100 ml stainless steel autoclave was used as the copolymerization reactor.

3.2.5 Schlenk line

Schlenk line consists of vacuum and argon lines. The vacuum line was equipped with the solvent trap and vacuum pump, respectively. The argon line was connected with the trap and the mercury bubbler that was a manometer tube and contain enough mercury to provide a seal from the atmosphere when argon line was evacuated. The Schlenk line was shown in Figure 3.2.
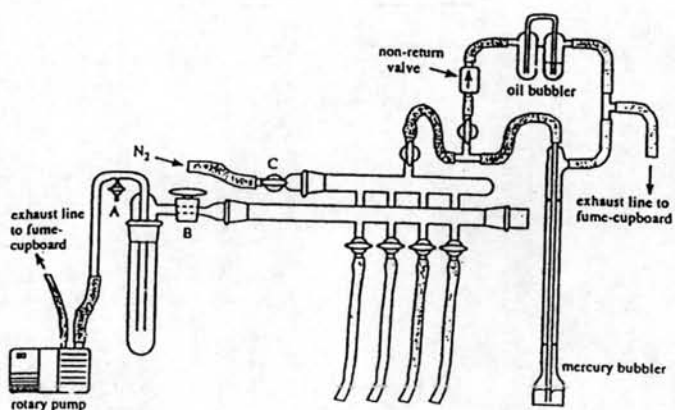
Figure 3.2 Schlenk line

3.2.6 Schlenk tube

A tube with a ground glass joint and side arm, which was three-way glass valve as shown in Figure 3.3. Sizes of Schlenk tubes were 50, 100 and 200 ml used to prepare catalyst and store materials which were sensitive to oxygen and moisture.
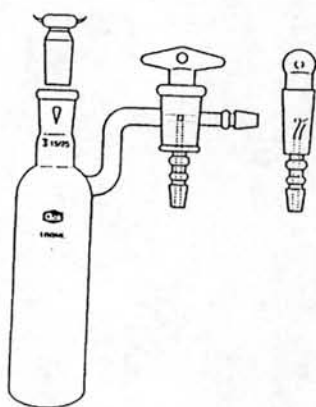

Figure 3.3 Schlenk tube

3.2.7 Vacuum pump

The vacuum pump model 195 from Labconco Corporation was used. A pressure of 10^{-1} to 10^{-3} mmHg was adequate for the vacuum supply to the vacuum line in the Schlenk line.
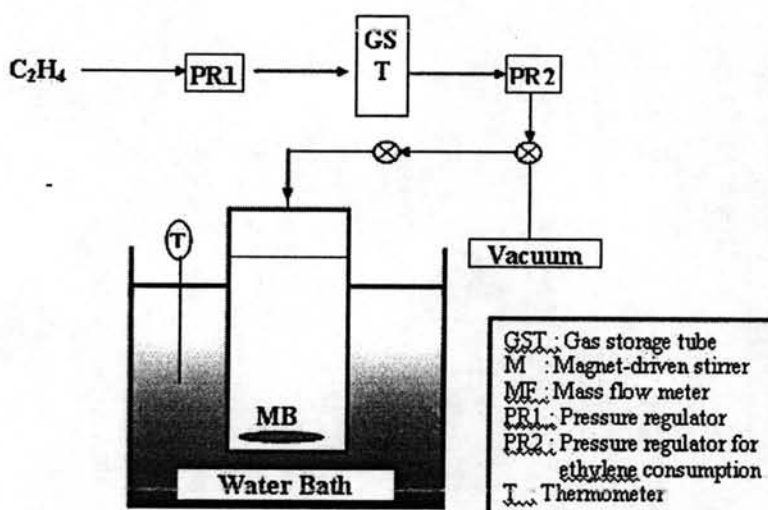
3.2.8 Polymerization line

Figure 3.4 Diagram of system in slurry phase polymerization

3.3 Characterizing instruments

The instruments used for characterizing catalysts and ethylene/α-olefin copolymer products are specified below.

3.3.1 Differential scanning calorimetry (DSC)

The melting temperature of ethylene/α-olefin copolymer products was determined with NETZSCH DSC 204 F1 at Scientific Technological Research Equipment Center, Chulalongkorn University. The analyses were performed at the heating rate of 10 °C/ min in the temperature range of 20-120 °C. The heating cycle was run twice. In the first scan, samples were heated and the cooled to room temperature. In the second, samples were reheated at the same rate, but only the results of the second scan

were reported because the first scan was influenced by the mechanical and thermal history of samples.

3.3.2 Gel permeation chromatography (GPC)

Molecular weight and molecular weight distribution of the produced ethylene/α-olefin copolymer were measured at 150 °C using 1,2-dichlorobenzene as solvent by a gel permeation chromatography at Thai Petrochemical Industry Public Company Limited. The GPC instrument was equipped with a PL-GPC 220 Differential refractometer (DRI), PL-BV 400 capillary bridge viscometer (Visc) and 2xPLgel 10 um MIXED-B (300x7.5mm) with PLgel 10 um guard (50 x 7.5 mm). The columns were calibrated with standard narrow molar mass distribution polystyrenes and linear low density polyethylene and polystyrene.

3.3.3 N₂ physisorption

Measurement of BET surface area, average pore diameter and pore size distribution of MCM-41 support were determined by N_2 physisorption using a Micromeritics ASAP 2000 automated system

3.3.4 Nuclear magnetic resonance (NMR)

The ^{13}C-NMR spectra were recorded at 100°C using JEOL JNM-A500 operating at 125 MHz. Copolymer solutions were prepared using 1,2 -dichlorobenzene as solvent and benzene-d_6 for internal lock.

3.3.5 Scanning electron microscope (SEM) and energy dispersive X-ray spectroscopy (EDX)

SEM observation with a JSM-5800 LV Scanning Microscope, Microspec WDX at Scientific Technological Research Equipment Center, Chulalongkorn University was employed to investigate the morphology of catalyst precursor and polymer. The polymer samples for SEM analysis were coated with gold particles by ion sputtering device to provide electrical contact to the specimen. EDX was performed using Link Isis series 300 program.

3.3.6 Thermogravimetric analysis (TGA)

TGA was performed using TA Instruments SDT Q 600 analyzer. The samples of 10-20 mg and a temperature ramping from 298 to 500 K at 2 K/min were used in the operation. The carrier gas was N_2 UHP

3.3.7 Raman spectroscopy

The Raman spectra of the samples were collected by projecting a continuous wave YAG laser of Nd (810 nm) through the samples at room temperature. A scanning range of 100-1000 cm^{-1} with a resolution of 2 cm^{-1} was applied.

3.3.8 X-ray diffraction (XRD)

XRD was performed to determine the bulk crystalline phases of sample. It was conducted using a SIEMENS D-5000 X-ray diffractometer with $CuK_\alpha(\lambda = 1.54439 \times 10^{-10}$ m). The spectra wrer scanned at a rate 2.4 degree/min in the range $2\theta = 20$-80 degrees.

3.3.9 X-ray photoelectron spectroscopy (XPS)

XPS was used to determine the binding energies (BE) and surface concentration of samples. It was carried out using the Shimazu AMICUS with VISION 2-control software. Spectra were recorded at room temperature in high-resolution mode (0.1 eV step, 23.5 eV pass energy) for Al 2p core-level region. The samples were mounted on an adhesive carbon tape as pellets. The energy reference for Ag metal (368.0 eV for $3d_{5/2}$) was used for this study.

3.4 Supporting Procedure

3.4.1 Preparation of dried-MMAO (dMMAO)

Removal of TMA from MMAO was carried out according to the reported procedure [24]. The toluene solution of MMAO was dried under vacuum for 6 h at room temperature to evaporate the solvent, TMA, and Al(iBu)$_3$ (TIBA). Then, continue to dissolve with 100 ml of heptane and the solution was evaporated under vacuum to remove

the remaining TMA and TIBA. This procedure was repeated 4 times and the white powder of dried MMAO (dMMAO) was obtained.

3.4.2 Preparation of bimodal MCM-41 support

The MCM-41 support was synthesized according to the method described by Panpranot et al. [23] using the gel composition of CTABr : 0.3 NH$_3$: 4 SiO$_2$: Na$_2$O : 200 H$_2$O, where CTABr denotes cetyltrimethyl ammonium bromide. Briefly, 20.03 g of colloidal silica Ludox HS 40 % (Aldrich Chemical Company, Inc.) was mixed with 22.67 g of 11.78 % sodium hydroxide solution. Another mixture comprised of 12.15 g of CTABr (Aldrich Chemical Company, Inc.) in 36.45 g of deionized water, and 0.4 g of an aqueous solution of 25 % NH$_3$. Both of these mixture were stirred by agitator for 30 min, then heated statically at 373 K for 5 days. The obtained solid material was filtered, washed with deionized water until no base was detected and then dried at 373 K. The sample was then calcined in flowing nitrogen up to 823 K (1-2 K/min), then in air at the same temperature for 5 h. After preparation, the unimodal MCM-41 support (denoted as UMD) having the pore diameter of ca. 2 nm and surface area of 864 m^2/g was obtained. The bimodal MCM-41 having average pore diameters of ca. 5 and 6 nm (denoted as BMD1 and BMD2, respectively) was prepared by treating the UMD-MCM-41 (before calcination) with an emulsion containing *N,N*-dimethyl decylamine (0.625 g in 37.5 g of water for each gram of MCM-41) for 3 and 4 days at 393 K. This was washed thoroughly, dried and calcined in flowing nitrogen up to 823 K (1-2 K/min), then in air at the same temperature for 5 h.

3.4.3 Preparation of MCM-41-supported dMMAO

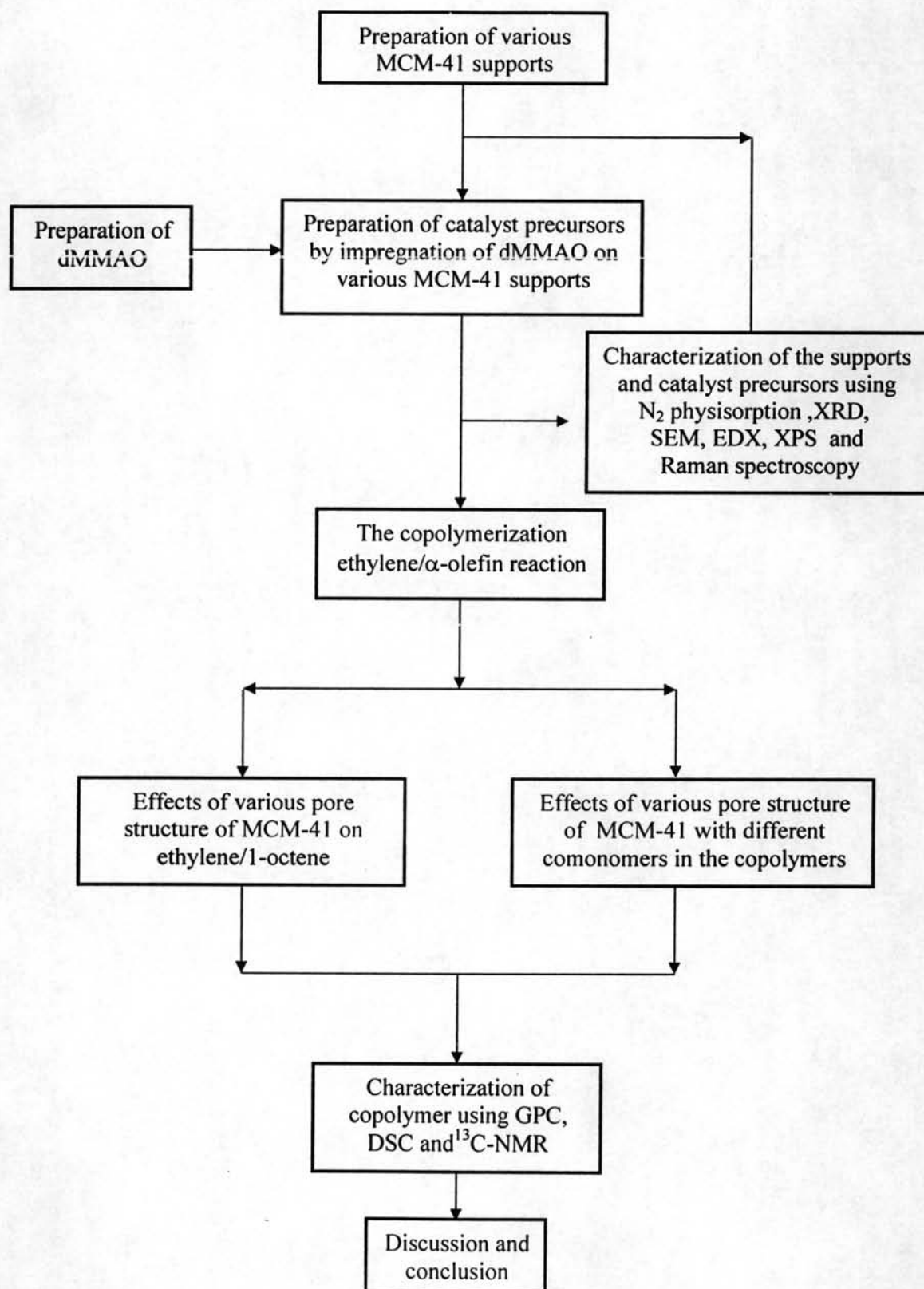The MCM-41 support was reacted with the desired amount of dMMAO in 20 ml of toluene at room temperature for 30 min. The solvent was then removed from the mixture by evacuated. This procedure was done only once with toluene (20 ml x 1) and 3 times with hexane (20 ml x 3). Then, the solid part was dried under vacuum at room temperature. The white powder of supported cocatalyst (dMMAO/support) was then obtained.

3.5 Ethylene and α-olefins copolymerization procedure

The ethylene and α-olefins (1-hexene, 1-octene and 1-decene) copolymerization reactions were carried out in a 100 ml semi-batch stainless steel autoclave reactor equipped with magnetic stirrer. The autoclave and magnetic bar were dried in oven at 110 °C for 30 minutes and purged with argon 5 times in glove box before use in copolymerization of ethylene and α-olefins. Toluene (to make a total volume of 30 ml), 100 mg of catalyst precursor, 3 ml of α-olefins were introduced into the autoclave in the glove box. The amount of $Et(Ind)_2ZrCl_2$ and TMA were mixed and stirred for 5 minutes at room temperature. After that, the mixture of metallocene and TMA was injected into the reactor. The reactor was frozen in liquid nitrogen to stop reaction and then the autoclave was evacuated to remove the argon. After that, the reactor was heated up to polymerization temperature and the polymerization was started by feeding ethylene gas (total pressure 50 psi) until the consumption of ethylene 0.018 mol (6 psi was observed from pressure gauge). The small amount of ethylene was used to avoid the mass transfer effect and increase the homogeneity of polymer. If the amount of comonomer remained higher than 90% after the reaction, the obtained polymer is homogeneous. The reaction of polymerization was terminated by addition of acidic methanol. The time of reaction was recorded for purposes of calculating the activity. The precipitated polymer was washed with methanol and dried in room temperature.

The various effects on the ethylene/α-olefins copolymerization with silica-supported metallocene catalyst and optimized condition were investigated. The effects of copolymerization on production of ethylene/α-olefins copolymer were systematically varied as follow.

3.6 Research methodology

```
                    ┌─────────────────────┐
                    │ Preparation of various│
                    │   MCM-41 supports    │
                    └─────────────────────┘
```

┌──────────────┐   ┌──────────────────────────┐
│ Preparation of│ ───▶ │ Preparation of catalyst precursors│
│   dMMAO   │   │ by impregnation of dMMAO on│
└──────────────┘   │ various MCM-41 supports │
                      └──────────────────────────┘

┌────────────────────────────────┐
│ Characterization of the supports │
│ and catalyst precursors using   │
│ N$_2$ physisorption ,XRD,   │
│ SEM, EDX, XPS and   │
│ Raman spectroscopy   │
└────────────────────────────────┘

┌──────────────────────┐
│ The copolymerization │
│ ethylene/α-olefin reaction│
└──────────────────────┘

┌──────────────────────┐   ┌──────────────────────┐
│ Effects of various pore│   │ Effects of various pore structure│
│ structure of MCM-41 on │   │ of MCM-41 with different│
│   ethylene/1-octene   │   │ comonomers in the copolymers│
└──────────────────────┘   └──────────────────────┘

┌──────────────────────┐
│ Characterization of │
│ copolymer using GPC, │
│ DSC and ^{13}C-NMR │
└──────────────────────┘

┌──────────────────┐
│ Discussion and   │
│ conclusion   │
└──────────────────┘

3.7 Characterization of supports and catalyst precursor

3.7.1 Pore size and pore size distribution

N_2 adsorption-desorption method was used to determine the BET surface area, average pore diameter and pore size distribution of MCM-41 supports

3.7.2 Morphology and elemental distribution

Scanning electron microscopic (SEM) and energy dispersive X-ray spectroscopy (EDX) technique was the effective method to investigate catalyst precursor morphologies and elemental distribution throughout the sample granules, respectively. The term of morphology was referred to shape, texture or form of supports and catalyst precursor.

3.7.3 The amount of Al on catalyst precursors

X-ray photoelectron spectroscopy (XPS) technique was used to determine the binding energies (BE) and surface concentration of catalyst precursor.

3.8 Characterization of ethylene and α-olefins copolymer products

3.8.1 Chemical structure determination

The nuclear magnetic resonance technique was widely used for characterizing incorporated comonomer. Comparison of the position of peak in the ^{13}C-NMR spectrum of polymer sample led to identification of the sequences of the comonomer incorporation.

3.8.2 Melting Temperature (T_m)

Differential scanning calorimetry (DSC) was an instrument designed to measure the thermal properties especially melting temperature (Tm). The melting temperature of ethylene/α-olefins copolymers were determined from the critical point of DSC curve.

3.8.3 Average molecular weight and molecular weight distribution

One of the most widely used methods for the routine determination of molecular weight (Mw) and molecular weight distribution (MWD) was gel permeation chromatography (GPC), which employed the principle of size exclusion chromatography

(SEC) to separate samples of polydispersed polymers into fractions of narrower molecular weight distribution.