

CHAPTER 2

EXPERIMENTAL

2.1 SYNTHESIS OF CATALYSTS

2.1.1 Materials and Glassware

Commercial chromium(III) nitrate nonahydrate, potassium persulphate, sodium thiosulphate, potassium iodide, silver nitrate and concentrated sulphuric acid were purchased from R&M Chemicals Ltd. The chromium(III) nitrate salt was kept in dry box to prevent moisture. Toluene, chloroform, concentrated hydrochloric acid, glacier acetic acid and chloro-substituted acetic acids were purchased from Merck. All the chemicals and solvents were analytical grade and were used as received. All the glassware were cleaned thoroughly before used. Flat bottom flasks and magnetic stirrers were kept in the drying oven. Figure 2.1 showed the reflux set up for the synthesis of chromium(III) complexes.



Figure 2.1: Apparatus set-up for the synthesis of chromium(III) complexes

2.1.2 Synthesis of Chromium(III) Oxo-Trinuclear Carboxylate Complexes

The complexes of chromium(III) with acetic acids, and substituted acetic acids were prepared by modifications of known methods^{1,2}.

Chromium(III) oxo-trinuclear carboxylate complexes were synthesized by reacting chromium(III) salts of nitrate with an excess of carboxylic acids.

(a) Chromium(III) Monochloroacetate Complex,



Mixture of chromium(III) nitrate nonahydrate, $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and monochloroacetic acid (solid, m.p. 62-64°C) at molar ratio of 1:10 was refluxed for 8 hours. Brown fume of NO_2 was evolved after an hour. The hot green solution was filtered at once and left to cool to room temperature. Green powdery product was formed upon cooling. Excess of monochloroacetic acid was removed by washing with chloroform. The product was dried in a vacuum oven at 60°C for 1 day. They were then stored in a desiccator.

(b) Chromium(III) Dichloroacetate Complex,



Chromium(III) nonahydrate and dichloroacetic acid and in a ratio of 1:13 were heated to melt and then refluxed for 15 hours. Brown fume was evolved during the reaction. The green solution obtained was filtered and cooled to room temperature. It was concentrated by prolonged standing for 2 weeks and a green product was obtained. Excess dichloroacetic

acid was removed by washing with chloroform and the complex was dried in vacuum oven at 60 °C for 1 day.

(c) Chromium(III) Trichloroacetate Complex,



Interaction between chromium(III) nitrate and trichloroacetic acid salt gave trichloroacetate chromium(III) complex. The complex was easily obtained by refluxing the reagents in the ratio of 1:6 for 10 hours. Green product was formed during synthesis.

The complex was filtered and washed with chloroform to remove excess trichloroacetic acid. The products were dried in the vacuum oven at 60°C for 1 day.

(c) Chromium(III) Acetate Complex,



Chromium(III) nitrate salt was refluxed with glacial acetic acid, CH₃COOH at a ratio of 1:13 for 13 hours. Brownish fume was evolved during the reaction. Green solution was obtained after the reaction and it was filtered hot at once. The solution was then allowed to cool to ambient temperature. Dark green solids formed upon cooling. The product was filtered and washed with chloroform to remove excess acetic acid. The green complex was dried in vacuum oven overnight at 60°C.

2.1.3 Analysis of Chromium Complexes

(a) Titrimetric method

The chromium content of each complex can be analyzed by a titrimetric method²⁻³. About 0.20g complex was first decomposed by treating it with concentrated sulphuric acid, H_2SO_4 . The chromium content was determined iodometrically after oxidizing Cr^{3+} to Cr^{6+} with potassium persulphate, $K_2S_2O_8$. The solution was treated with 2ml silver nitrate solution (0.10M) to precipitate the chloride ions in the system before excess potassium persulphate solution was added to the solution mixture. Next, the solution mixture was boiled gently for 20 minutes to oxidize Cr^{3+} to Cr^{6+} (catalyzed by Ag^+) and also destroy the excess $K_2S_2O_8$. The orange solution obtained was cooled to room temperature. 10ml sulphuric acid (10%) and 2ml phosphoric acid (10%) were added to acidify the solution. 10ml concentrated hydrochloric acid (HCl) was then added followed by 1.00g potassium iodide, KI and the mixture was titrated against standardized sodium thiosulphate solution (0.05M). From the molar concentration of chromium solution obtained by titration, the chromium content in the complex can then be calculated.

(b) FT-IR Spectroscopy

FT-IR spectra were recorded on a Perkin Elmer Spectrometer model 1600. The chromium complex was first mixed with KBr powder at approximately 1:100 and pressed into disc. The spectra were scanned in the range of $4000-400cm^{-1}$.



Figure 2.2: Perkin Elmer Fourier Transform Infrared (FT-IR)
Spectrometer model 1600

(c) Thermal Analysis

Determination of chromium as its oxide was carried out with TGA. The analysis was performed using a Perkin-Elmer TGA7 system. Measurement was made on sample (about 10mg) under nitrogen atmosphere in the temperature range of 50-1000°C and at a heating range of 20°C min⁻¹.



Figure 2.3: Perkin-Elmer TGA7

2.2 POLYMERIZATION AND COPOLYMERIZATION

2.2.1 Materials and glassware

High purity ethylene and propylene (99.9%) were purchased from Malaysian Oxygen Ltd Company. They were dried by passing through successive columns containing activated 3A molecular sieve and sodium hydroxide pellets. Toluene was purified by distilling over sodium metal under N₂ atmosphere. The distilled toluene was kept dry in a stoppered bottle over activated molecular sieves (3A).

The synthesized chromium complexes were ground and kept in desiccators. AlEt₂Cl obtained from Aldrich Chemical Company was used as cocatalyst. 0.1546M of the cocatalyst was prepared in the nitrogen filled dried box using distilled and dried nitrogen as solvent.

Due to sensitivity of cocatalyst to trace impurities, therefore all glassware, syringes and needles were cleaned thoroughly in an ultrasonic bath (Sonorex, model no.RK100) for at least 15 minutes. They were dried in oven at 120°C after washing and rinsing with distilled water. The gas line was evacuated and flushed with ethylene gas prior to polymerization.



Figure 2.4: Polymerization gas line with constant volume set-up

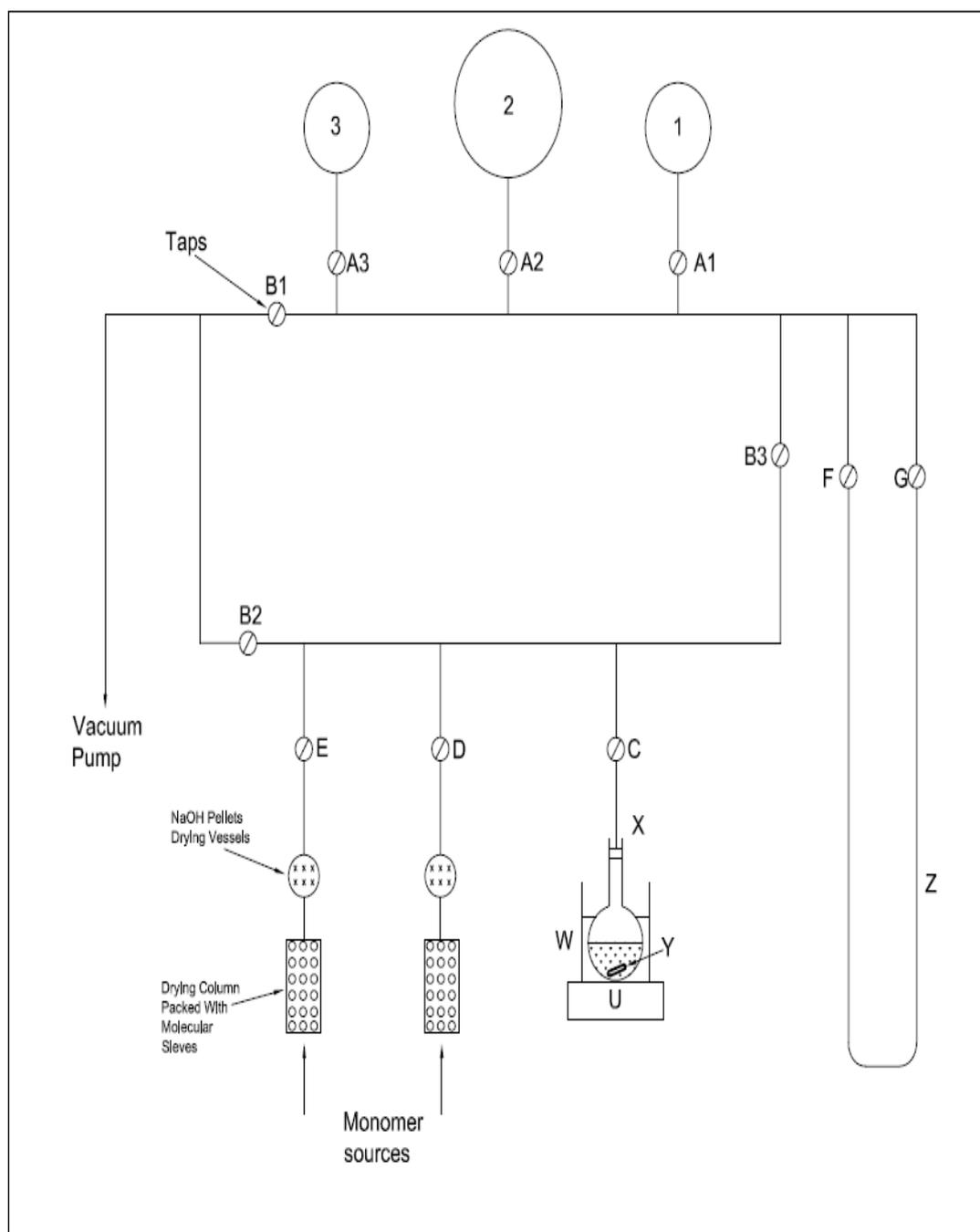


Figure 2.5: Schematic diagram of polymerization gas line.

Reservoirs 1, 2 and 3 are used to store monomer;
 U, hotplate; W, thermostated water bath; X, reactor;
 Y, magnetic stirrer; Z, monomer;

Taps A1, A3, B3, C and G are opened during polymerization.

2.2.2 Constant Volume Setup

Diagram of the polymerization gas line is presented in Figure 2.4 and Figure 2.5. Before the reservoir flasks were joined onto the line, the volumes have been calibrated by filling water into the reservoirs². The volumes of reservoirs 1, 2 and 3 were 1094ml, 4257ml and 1104ml respectively.

Ideal Gas Law $PV=nRT$ was used to determine the dead volume of the polymerization line. Firstly, tap A1 for reservoir flask 1 was closed and the gas line was evacuated to remove air. Then, gas line from tap C up to A1 was allowed to fill with air and initial pressure, P_1 was noted. Tap A1 was then opened to let the air fill in reservoir 1 and final pressure, P_2 was recorded. The procedure was repeated with reservoir flasks 2 and 3.

Assuming $P_1V_1 = P_2V_2$ at constant temperature and $V_2 = v + V_1$, where v is the volume of reservoir flask and V_1 is the 'dead volume' of the gas line.

$$P_1V_1 = P_2(V_1 + v)$$

$$V_1(P_1 - P_2) = P_2v$$

$$V_1 = \frac{P_2v}{(P_1 - P_2)}$$

Table 2.1: Determination of 'dead volume' of the gas line

Reservoir flask	Volume of flask, v/ml	Initial pressure, P_1 /cmHg	Final pressure, P_2 /cmHg	Dead volume, V_1 /ml
1	1094	76.00	25.60	556
2	4257	76.00	8.90	565
3	1104	76.00	25.50	557

Table 2.1 shows the 'dead volume' determined using different reservoir flasks and the average 'dead volume' of the gas line is $559 \text{ ml} \pm 6 \text{ ml}$. In a typical experiment, normally only reservoirs 1 and 3 were used, hence the total volume of the reservoir flasks was 2198 ml. The volume of reactor used was 340 ml and the quantity of toluene solvent was 100 ml. Therefore the total volume occupied by monomer gas for polymerization was 2997 ml.

2.2.3 Ethylene Polymerization

Ethylene polymerization was carried out at room temperature using a gas line with a constant volume setup. Before the experiment starts, the gas line was evacuated and the system was flushed with monomer gas to remove any impurities. Monomer gas filled in the gas line through tap D.

About 0.02g catalyst was weighed and was transferred into a 250ml round bottom flask. The reaction flask was then loaded with toluene (solvent) followed by the required amount of AlEt_2Cl (cocatalyst). The cocatalyst was being diluted to the concentration of 0.1546M before it was added into the flask by means of graduated syringe. The total volume of the solvent and cocatalyst was maintained at 100ml. The mixture was left to 'age' for 15 minutes before introducing the monomer gas. Due to the mixture order of catalyst and cocatalyst affects the polymerization result⁴⁻⁵, the polymerization mixtures were added in same order to obtain reproducible results. The reaction vessel was stoppered, removed from the dry box and connected to the gas line at C as shown in Figure 2.5.

During ethylene polymerization process, only reservoir flasks 1 and 3 were used. Both the reservoirs were filled with monomer gas through taps A1 and A3 while taps A2 , B1 and B2 were closed. After that, tap C was opened to introduce ethylene gas into the

reaction vessel. The stirrer was turned on and maintained at a constant stirring speed throughout the reaction. The rate of polymerization was monitored by reading the monomer pressure drop using mercury manometer in units of cmHg. The polymerization reaction was carried out for 1 hour unless stated otherwise.

At the end of the polymerization run, tap C was closed and the reaction vessel was disconnected from the gas line. The line was evacuated in order to remove remaining monomer gas. The content was poured into 400ml methanol acidified with 5ml concentrated hydrochloric acid in order to quench the reaction. The mixture was left to stir for a few hours. Later, the polymer precipitate was filtered with a sintered glass and was thoroughly washed with methanol. The product was then dried overnight in vacuum oven at 60°C. The yield was noted.

2.2.4 Propylene Polymerization

Polymerization run was carried out under the same conditions as described earlier in Section 2.2.3 except the monomer gas was changed to propylene gas. The gas line was filled with propylene gas through tap E.

After the polymerization, the reaction flask was disconnected from the gas line. The products were poured into a beaker containing 400ml methanol acidified with 5ml concentrated HCl. The mixture was stirred for a few hours at room temperature. Very little white precipitation was observed after the stirring. The solution was left to evaporate in the fume cupboard.

2.2.5 Stirring Speed

Earlier works had shown that stirring speed could affect the rate of reaction^{6-7,9}. Therefore, it is essential to take precaution step to ensure constant stirring speed by setting the stirrer at the same marking for all the polymerization run. For heterogeneous catalysts presumably the rate of monomer gas to reach the solid active sites of the catalysts was diffusion controlled.

2.2.6 Grinding The Catalyst

In heterogeneous catalyst, the efficiency of a catalyst is dependent on its physical state. Grinding the catalyst could increase the activity of the heterogeneous catalyst¹⁰ presumably smaller particle size lead to higher surface area thus provide more active centres for reaction. Catalysts used in this project were ground finely and were kept in dessicator.

2.2.8 Characterization of Polymers

In the synthesis of polymers, relationship between the properties of polymers and their chemical structure must not be neglected. Thus, polymer characterization has a goal to improve the performance of the product. Since the development of Ziegler-Natta catalysts¹¹⁻¹⁵, polyolefins such as polyethylene and polypropylene with desirable properties and structures have been successfully made. Techniques used to characterized polymers include infrared spectroscopy, differential scanning calorimetry (DSC), nuclear magnetic resonance (NMR), gas chromatography, X-ray diffraction and scanning electron microscopy (SEM).

In this study, polyethylene and polypropylene obtained were characterized using Fourier Transform Infrared (FT-IR) spectroscopy, attenuated total reflection infrared (ATR) spectroscopy and differential scanning calorimetry (DSC).

Absorption spectroscopy¹⁶ has been utilized to characterize the chemical structure of polymers such as determination of the various olefinic groups, crystallinity measurements and polyethylene branching studies. Infrared spectroscopy^{8-9,17} is the most common technique of absorption spectroscopy being used in the characterization of polymers. It detects the vibration characteristics of chemical functional groups in a sample. A Fourier Transform Infrared (FT-IR) Spectrometer¹⁸⁻¹⁹ detects IR radiation when it passes through a polymer sample. The resulting spectrum provides information on the molecular absorption and transmission. FT-IR can be used to determine the amounts of component in a polymer and identify unknown compounds.

Another common type of the infrared spectroscopy used is attenuated total reflection infrared (ATR-IR) spectroscopy²⁰⁻²¹. The first applications of attenuated total reflection (ATR) were reported independently by Fahrenfort and Harrick. ATR spectroscopy analyses the surface of materials. The benefit of ATR-IR spectroscopy over FT-IR spectroscopy is the ability to characterize materials which are too thick.

Differential scanning calorimetry, DSC²² is a thermoanalytical technique to study the properties of polymers such as melting, crystallization, glass transitions and degree of crystallinity. DSC is one of the easiest analytical techniques to use as it only requires minimal sample preparation and quantitative information can be obtained from only a few milligrams of materials.

(a) Infrared Spectroscopy

(i) FT-IR Spectroscopy

Polymer samples were pressed into thin film by Carver hot press at temperature between 100°C and 130°C for 20-30 seconds. The samples were placed between aluminium foil before pressing. The pressure applied was 8-9 tons. The thin layer obtained was cooled to room temperature. The samples were mounted onto a cardboard holder and their spectra were recorded by Perkin-Elmer Spectrum RX1 FT-IR spectrophotometer within the range 500-4000cm⁻¹. The recorded spectra were then analyzed by Perkin-Elmer FT-IR software.

(ii) ATR-IR Spectroscopy

Firstly, infrared transmitting crystal on the Perkin-Elmer Spotlight 400 ATR-IR spectrometer was cleaned thoroughly. Polymer samples were then placed on the crystal and force was applied onto the samples. The samples were scanned through the spectrometer at mid-infrared region (650-1000cm⁻¹). The spectra obtained were analyzed using Perkin-Elmer ATR-IR software.

(b) Differential Scanning Calorimetry (DSC)

2-3 mg of polymer samples were encapsulated in an aluminium sample pan and their weight was recorded. Calorimetric measurements for the samples were obtained using a Perkin-Elmer Differential Scanning Calorimeter, DSC 7. Polymer samples were heated to 150°C at the rate of 10°C/min. They were held isothermally for 10 minutes before cooling back to initial temperature (35°C) at the rate of 5°C/min. The samples were annealed for 5 minutes at 35°C and were then heated to 150°C at 10°C for the second time.

Referring to the DSC curve, the enthalpy change (ΔH) of the polymers can be calculated from the area under each peak. The endothermic peak shows melting temperature (T_m) of the samples while crystallization temperature (T_c) can be obtained from the exothermic peak.



Figure 2.6: Perkin-Elmer Differential Scanning Calorimeter, DSC 7

2.2.9 Ethylene and Propylene Copolymerization

The constant volume setup for copolymerization of ethylene and propylene was the same as homopolymerization of ethylene and propylene. The polymerization gas line was shown in Figure 2.5.

Firstly, the polymerization gas line was evacuated. Known volume of ethylene and propylene monomers were then separately introduced into reservoirs 1 and 3 respectively. Initial pressures of the two monomers were noted. The reservoir taps were opened to allow

the monomer gases to mix for 1 hour. The total initial pressure was obtained from the manometer reading.

Ethylene-propylene copolymerization was carried out in a 250ml round bottom flask at room temperature. About 0.02g catalyst and toluene were transferred into the reaction flask. Required amount of AlEt_2Cl (cocatalyst) was then added to make up to 100ml. The reaction vessel was stoppered, removed from the dry box and connected to the gas line. The mixture was left to 'age' for 1 hour before introducing the monomer gas.

After 1 hour, tap C which connected to the reaction flask was opened to introduce the mixture of ethylene and propylene monomers into the flask. The magnetic stirrer was turned on and copolymerization reaction was carried out for 1 hour. Pressure drop during the reaction was recorded. Copolymerization was terminated by adding acidified methanol. The product was washed with methanol and was dried overnight in vacuum oven at 60°C .

2.2.10 Characterization of Copolymer

Ethylene-propylene copolymers obtained were characterized using FT-IR spectroscopy and DSC. The analysis procedures were described in Section 2.2.8.

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