Chapter III: Ethylene polymerization: Experimental

3.1 Materials

3.1.1 Reagents

All the reagents used in the experiments (except catalysts) are listed in Table 3.1. All air-sensitive compounds were handled and stored in a LABCONCO glovebox under high purity argon atmosphere.

The molecular sieves 3Å were baked in furnace at 400 ^{o}C for 8 hours and were cooled down to room temperature in a dry atmosphere prior to use.

Toluene (A. R. grade, > 99% purity) was further purified by refluxing over sodium metal, then distilling under nitrogen atmosphere. It was then kept dried in a stopper bottle over activated molecular sieves 3Å after degassing with nitrogen bubbling in order to remove moisture and oxygen through it. Approximately 600 grams of activated molecular sieve 3Å were added to 4 L of purified toluene and kept in the dry atmosphere at least 12 hours prior the polymerization.

Methanol and isopropyl alcohol were purified by simple distillation prior to use.

All other reagents were used as purchased without further purification.

Table 3.1 Specification of the reagents used in experiments

Name	Chemical Formula	Grade	Supplier
Toluene	$C_6H_5CH_3$	> 99% purity	J. T. Baker
Diethylaluminum chloride	$AlEt_2Cl$	9M in toluene	Sigma-Aldrich
Hydrochloric acid	HCl	37% ACS reagent	R&M
1,2,4 Trichlorobenzene	$C_6H_3Cl_3$	99% purity	ACRŌS
Methanol	CH_3OH	Distilled	R&M
Isopropyl alcohol	C_3H_7OH	Distilled	R&M
Potassium hydroxide	KOH	pellets	R&M
Molecular sieves 3Å	-	3.2 mm particle size	Sigma-Aldrich
Deuterated benzene	C_6D_6	99.6% for NMR	MERCK
Liquid nitrogen	LN_2	-	MOX-LINDE

3.1.2 Glasswares and reactor

Knowing that traces of impurities could affect the rate of the polymerization by reacting with the cocatalyst ($AlEt_2Cl$) which is sensitive to moisture and air (oxygen, water), extreme care was taken during cleaning.

All glassware was soaked overnight in a solution of potassium hydroxide / isopropyl alcohol (20% w/v). They were then transferred into a top ultrasonic cleaner, (model POWER SONIC 405) and cleaned for at least 20 minutes, before washing and rinsing appropriately with distilled water. They were then dried in a 100^oC oven for at least 24 hours prior cooling at ambient temperature in the argon atmosphere dry box.

Disposable syringes (TERUMO Syringe), were kept in the purified argon atmosphere glovebox for at least 12 hours prior to used.

The 1 L autoclave reactor from Parr Industries, used in these studies, was washed and rinsed thoroughly with distilled water. It was further dried in a 100^oC oven for at least 15 hours prior to use.

3.1.3 Gases

Nitrogen, ethylene and argon were the only gases used in the experiments. They were all used without further purification. Nitrogen was employed to distill and purge the polymerization medium (toluene), to purge the polymerization reactor and to transfer the polymerization solution in the reactor. Argon was used to provide an inert atmosphere in the dry box. Table 3.2 shows the specification of these gases.

Table 3.2: Specification of the gases used in experiments

Name	Formula	Grade	Supplier
Ethylene	C_2H_4	99.9% purity	LINDE Singapore
Nitrogen	N_2	Industrial	MOX-LINDE
Argon	Ar	99.9% purity	MOX-LINDE

3.1.4 Catalysts

$[Cr_3O(CCl_3CO_2)_6.2H_2O]CCl_3CO_2.3H_2O$ and $[Cr_3O(F_3CCOO)_6.3H_2O]NO_3.H_2O$ complexes were used for the polymerization experiments. Their synthesis and characterization have been detailed in chapter two. Both compounds are stable at ambient temperature. They were ground finely and kept in a vacuum desiccator prior to use. Grinding the complexes would improve their surface area and hence, probably produced more active site for the polymerization. Hence the increase in the initial activity of the catalyst would be observed [1-4].

3.2 Polymerization procedure

All procedures were performed under inert atmosphere (argon) in a LABCONCO dry box or using standard Schlenk techniques.

The polymerization experiments were carried out in a 1 L stainless steel autoclave reactor equipped with a mechanical stirrer and a control panel containing a pressure transducer (calibrated by the manufacturer) and temperature controller (Figure 3.1). However, excellent temperature control was achieved by replacing the heating mantle of the reactor (Parr industries) by a water bath equipped with thermoregulator as the temperature was maintained within (40 ± 3) ^oC. Data were collected on a computer, connected to the control panel through digital to analog (D/A) and analog to digital (A/D) boards

Before the polymerization, the reactor (1 L) was dried at 100 ^oC for at least 15 hours and cooled to room temperature. In addition, it was evacuated and flushed with nitrogen gas several times, then pressurized with ethylene to 60 psi at least three times to remove oxygen and moisture.

All polymerization solutions were prepared in the same manner in order to get reproducible and comparable results. The desired amount of chromium(III) complex was weighed out and introduced into a 500 mL glass reactor. It was then introduced into the dry box where the required amount of polymerization medium (dried toluene) and cocatalyst ($AlEt_2Cl$) were respectively transferred into it. The initial heterogeneous green solutions turned heterogeneous yellowish immediately after the cocatalyst was introduced. The total mixture (400 mL) was then placed into septum-sealed vials, removed from the dry box and stirred at low speed while waiting for the 40 minutes of ageing time.

After ageing time, the mixture is transferred under nitrogen pressure, through a cannula to the reactor, previously cooled within the temperature range of -50 to -10 ^oC. The reactor was then pressurized with ethylene to the desired pressure. Cooling the reactor will slow down any polymerization which occurs during the time the reactor is filled with the monomer. Once the desired pressure was reached, the ethylene supply was stopped and the polymerization was started by immersing the reactor in the water bath adjusted to the desired temperature. The stirrer speed was set to a constant average value of 300 rpm and the polymerization temperature was controlled by cooling the water bath, when necessary, with ice cubes. Ethylene consumption was recorded during polymerization by the computer equipped with the LABVIEW program. All polymerization runs were conducted, at constant temperature (40 ± 3) ^{o}C and variable pressures for 60 minutes. To terminate the reaction, the thermoregulator was switched off, the stirrer was stopped, the reactor was degassed and the polymer was precipitated with a mixture of 400 mL of methanol acidified with 5 mL of concentrated hydrochloric acid. The mixture was stirred for several hours and the precipitated polymer was isolated by filtering, then adequately washed with excess methanol and dried in vacuum at 50 ^{o}C until constant weight was achieved.

Figure 3.1: Layout of Parr Reactor

3.3 Polymer characterization

3.3.1 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared spectroscopy is a practical method for the characterization of various functional groups, quantitative studies, crystallinity measurements and branching studies of polymers. Infrared analyses were carried out using a Perkin Elmer spectrum 400 FT-IR / FT-NIR spectrometer. About 5-20 mg of sample was weighed and pressed into the instrument. 15 scans were used to collect each spectrum in the range of 4000 to 650 cm^{-1}. Then, spectra were analyzed by Perkin Elmer software equipped with a 2007 library of program.

3.3.2 Thermogravimetry Analysis (TGA)

TGA is a useful method applied to study the thermal stability of compounds. Thermogravimetric measurements were carried out using a Perkin Elmer thermogravimetric analyzer model TGA 6 with platinum pan. The curves were obtained over the temperature range 50-900 ºC under a nitrogen atmosphere (flow rate of 20 mL min^{-1}) with a heating rate of 10 ºC /min.

3.3.3 Differential Scanning Calorimetry (DSC)

DSC is a thermal method used to measure the enthalpy changes of a sample. By monitoring the changes in supplied energy against the temperature, the thermal transition of a polymer such as the heat of fusion or recrystallization and the glass transition point can be detected. For polyethylene, the degree of crystallinity can be estimated by comparing the measured melting enthalpy to that of a pure polyethylene crystal [5]. According to Xu et al. [6], the ΔH_f for a pure polyethylene crystal is estimated to be approximately 289 J/g. The melting transitions of polymers are very sensitive to their thermal history. Different crystalline structures are formed depending on the thermal treatment of the polymer either by slow quenching or annealing of the sample. The first temperature scan of DSC measurements is considered in case where we would like to discuss the effect of thermal history of the polymer. However, a better estimate of the inherent properties of the sample is to erase its thermal history by melting it in the first scan and then obtaining the thermal estimates from the second scan.

In these studies, calorimetric measurements were determined using a Perkin-Elmer DSC 6 differential scanning calorimeter. Indium was used for the calibration of the temperature scale. 5 – 10 mg of purified polyethylene sample were weighed and encapsulated into a standard aluminum sample pan. The samples were heated from 35 to 200 ^{o}C at 10 ^{o}C/min, annealed for 10 minutes, air cooled to 35 ^{o}C, wait for 10 more minutes before reheated from 35 ^{o}C to 200 ^{o}C at 10 ^{o}C/min. The melting point and the degree of crystallinity of the polymer were estimated from the second scan. The degree of crystallinity was estimated by comparing the DSC melting enthalpy to that of a perfect polyethylene crystal ($\Delta H \approx 289$ J/g).

3.3.4 Hardness test

Hardness is an unusual physical property. It is the result of a defined measurement procedure and not an intrinsic materials property. It is susceptible to precise definitions in terms of fundamental units of mass, length and time. It can be defined as the resistance to elastic deformation on the surface for elastomers and some polymers. The advantage of a hardness test is that it involves only a limited area for measurement thus the sample is relatively unaffected by the test [7-9]. In these studies, about 20 to 40 mg of samples were placed between aluminum foil and pressed using a Molding Test Press Tester (TMJ-8122B) for 5 to 10 seconds at temperature of 5 ^{o}C above their melting point. The pressure applied was about 20 bars. The sample was cool at room temperature before being pressed in a Wallace hardness tester model to record it hardness data. The measurement was repeated at least five times, in different areas for each sample, and the average value was considered as the hardness measurement.

3.3.5 Density test

The density of a polymer is its physical property which can be related to how closely pack the sample is. In a qualitative manner, it is defined as the measure of the weight of the material divided by its volume. Density can be used to calculate the crystallinity percent of a polymer. In the present studies, the resultant product (high density polyethylene), tend to a powder, making it difficult to calculate its volume. Thus, about 20 to 40 mg of each sample was placed between aluminum foil and pressed, using a Molding Test Press Tester (TMJ-8122B), for 5 to 10 seconds at a temperature 5 ^{o}C above its melting point. The pressure applied was about 20 bars. The sample, cooled down to room temperature, was placed in a 50 mL beaker. 15 mL of distilled water was poured into it and the mixture was gradually titrated with methanol while occasionally shaking. It was considered that the densities of the sample and the water / methanol mixture were identical when the plastic pieces remain suspended in the water / methanol solution. The densities of the mixtures were determined by pipetting and weighing them.

3.3.6 Dynamic Mechanical Analysis

DMA is frequently used to estimate the viscoelastic properties of a material in its solid state. It is well known that polymeric behaviors are temperature dependent. Polyethylenes, like other plastics, are hard and rigid at room temperature but become softer at high temperature. This hardness or stiffness is determined as a modulus, a ratio of stress to strain at a certain level of deformation. In these studies, only dynamic temperature sweeps were carried out.

Dynamic mechanical properties were measured out using a TA instrument DMA Q800 dynamic mechanical analyzer. Samples were placed and pressed with a spatula into rectangular bars (12.76 mm x 3.20 mm x 35 mm). Storage and loss moduli were obtained in dual cantilever mode over a temperature range of -140 ^oC to 40 ^oC, oscillation frequency of 1 Hz, and scanning rate of 3 ^oC/min. Liquid nitrogen was used to cool the sample and the relaxation modes of the polymers were calculated using loss modulus and tan δ curves. tan δ is the ratio of loss modulus (E”) and storage modulus(E'), thus large values of tan δ indicate greater energy loss while small values show a stiffer more elastic response.

3.3.7 Nuclear Magnetic resonance spectroscopy (NMR)

The NMR technique is one of the methods used to study the microstructure of polymers. In this work, ^1H and ^{13}C spectra were collected using a JEOL JNM-LA 400 FT-NMR system spectrometer. The solutions for analysis were prepared by heating (150 ^oC) about 150 – 200 mg of sample in a solution of 1,2,4 trichlorobenzene with deutereuted benzene (90/10 %, v/v). Analyses were carried out at 140 ^oC, processed with Lambda software and chemical shifts read in ppm with respect to the internal standard which is tetramethylsilane (TMS).

3.4 References

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