Chapter 2

Experimental

2.1. Materials

All work involving air and /or moisture-sensitive compounds was carried out by using standard high vacuum Schlenk or dry box (VAC) techniques shown in Fig. 2.1 in nitrogen atmosphere. Toluene and hexane were refluxed over sodium wire for 4h and distilled before use, using solvent purification system as shown in Fig. 2.2 [1]. Polymer grade ethylene was used directly from commercial plant, the pressure of which was adjusted with a two stage regulator. Co-catalysts were purchased from Ethyl Corporation or Witco GmbH and used without further purification. Titanium *tetra* iso-propoxide, titanium triisopropoxide chloride and titanium tetrachloride and the different biphenols were purchased from Aldrich & Merck and used without further purification.

2.2 Measurements

The analytical methods used to characterize the catalyst microstructure and physical properties of the polymer are described below.

Elemental Analysis

Microanalysis was carried out on a Perkin Elmer, Model 2400, CHN Analyzer, by decomposing the complex at high temperature and estimating the combustion product by TCD. The system was calibrated using acetonitrile supplied by Perkin Elmer prior to use. Titanium content in catalysts was determined gravimetrically as TiO_2.

Infrared Spectroscopy

A Perkin Elmer FT-IR spectrometer model Spectrum BX was used to obtain the IR spectra of samples pressed into KBr pellets over 4000 to 400 cm^{-1} range. The instrument was calibrated using polystyrene film supplied by manufacturer.

Nuclear Magnetic Resonance

The ^1H NMR spectrum of catalysts was recorded in $CDCl_3$ solvent on a Varian NMR 300 MHz spectrometer using TMS as an internal reference. ^{13}C NMR spectra was recorded using $CHCl_3$ and DMSO as a solvent.

FAB Mass Spectra

FAB mass spectral analysis of catalysts was carried out on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon as the FAB gas. The accelerated voltage was 10 kV and the spectra recorded at room temperature. *m*-nitrobenzyl alcohol was used as the matrix.

Size Exclusion Chromatography

Molecular weights of polymers were determined using size exclusion chromatography (SEC). The high temperature GPC analysis of the polymers was carried out using Polymer Lab's PL-GPC 220 chromatograph. A set of PL Gel three Mixed B columns were used. 1,2,4 Trichlorobenzene was used as the mobile phase at 135°C. 0.0125% Irganox was added to the mobile phase prior to filtration. A sample preparation unit, PL-SP260, was used to dissolve and filter the samples at 135°C. 0.2% solutions were injected with the help of an auto sampler to record the chromatogram. Viscotek's Trisec conventional software was used to analyse the chromatograms which were matched with polystyrene calibration curve. The following MHK constants were used to construct a universal calibration curve. For PS: $K= 1.2105e^{-4}$; $a = 707$; PE: $K = 4.055e^{-4}$; $a = 725$.

Differential Scanning Calorimetry

Differential Scanning Calorimetry was performed under continuous nitrogen purge on a Mettler-Toledo DSC 822 instrument from 30 to 200°C at a scan rate of 10 °C/min. Indium was used to perform the calibration of equipment.

Thermal Analysis

TGA/DTA of catalysts were recorded in air (heating rate 10°C/min) from ambient to 600°C on a TA Instrument (Universal V2).

Density of polymers was determined in n-butyl acetate medium at 23^0C as per ASTM method D 792-00.

X-ray diffraction

X-ray diffraction experiments were carried out on a Brüker AXS model D8 advanced diffractometer. Scattering patterns were obtained with Ni-filled CuKα radiation (λ =1.5406 A°, generator voltage = 45kV , current = 40 μA) in the reflection mode, detected by a scintillation counter. Samples were pressed films approximately 400μ thick and were scanned into 2θ ranges from 15°- 45° at a rate of 1°/min. Measurements were recorded at steps of 0.02°.

Scanning Electron Microscopy

Scanning electron micrographs of powdered polymer samples were taken on a JEOL JFC 1100 instrument ion sputter water. They were observed in JEOL 5600 CV Scanning Electron Microscope in Hv mode with operating voltage of 20 kV.

2.3. Catalyst Preparation

Different phenols and biphenols employed in this study are broadly classified as under:

a) Binol and its derivatives

b) 2,2' Biphenol and Substituted biphenols

c) Phenol and Substituted phenols

d) Sulphur bridged biphenol

For the catalyst preparation following three synthetic routes are well established and reported in the literature [2-5].

i) stoichiometric reaction between $Ti(OPr^i)_4$ and biphenol ligand (alcohol exchange) and separation of liberated *iso*-propanol by (azeotropic / vacuum distillation)

ii) treatment of a lithium salt of biphenol (LiOR—ROLi) with $TiCl_4$ followed by removal of LiCl

iii) low temperature reaction between the biphenol and titanium tetrachloride in presence of a triethylamine for eliminating the HCl formed

Catalysts **1-28** were synthesized by using the method (i) and in a few case method (iii) described above using an appropriate ligand depicted in Table 1 or reported in the literature. To a solution of 1 mmol of $Ti(OPr^i)_4$ in toluene (25 mL) was added slowly calculated quantity of the corresponding bi-phenol ligand in warm toluene (30 mL) under nitrogen atmosphere and heated at 60°C for 3 h. The contents were then stirred for 24 h at room temperature. The solvent was carefully removed under vacuum, precipitated solid washed with small portions of warm toluene and finally the orange coloured complexes were isolated. All catalysts are characterized by the techniques described above.

Table 1 List of Ti-complexes synthesized.

Catalyst No.	Ligand (L_n)	Ti Precursor (Ti)	L_n : Ti Molar Ratio	Method
1	1,1' binaphthalene 2,2' diol (Binol)	$Ti(OPr^i)_4$	2:1	i
2	Binol	$Ti(OPr^i)_4$	1:1	i
3	*R* Binol	$Ti(OPr^i)_4$	2:1	i
4	*S* Binol	$Ti(OPr^i)_4$	2:1	
5	6,6'-Bromo Binol	$Ti(OPr^i)_4$	2:1	i
6	Binol	$TiCl_4$	1:1	iii
7	Binol	Cp_2TiCl_2	1:1	iii
8	2,2'-Biphenol	$Ti(OPr^i)_4$	1:1	i
9	1,1' methylene di-2-naphthol	$Ti(OPr^i)_4$	1:1	i
10	2,2'methylene *bis* (4 chlorophenol)	$Ti(OPr^i)_4$	1:1	i
11	2, 2' methylene *bis*(6 *tert* butyl-4-ethyl phenol)	$Ti(OPr^i)_4$	1:1	i
12	2, 2' ethyledene *bis*(4,6-di *tert* butyl phenol)	$Ti(OPr^i)_4$	1:1	i
13	2, 2' methylene *bis*(4-methyl-6 *tert* butyl phenol)	$Ti(OPr^i)_4$	1:1	i, [6]
14	2, 2' methylene *bis*(4-methyl-6 *tert* butyl phenol)	$Ti(OPr^i)_4$	2:1	i, [6]
15	2, 2' methylene *bis*(4-methyl-6 *tert* butyl phenol)	$Ti(OPr^i)_3Cl$	1:1	i
16	2, 2' methylene *bis*(4-methyl-6 *tert* butyl phenol)	$TiCl_4$	1:1	iii, [6]

Catalyst No.	Ligand (L_n)	Ti Precursor (Ti)	L_n : Ti Molar Ratio	Method
17	Binol	$Ti(OPr^i)_3Cl$	1:1	i
18	1,1' methylenedi-2-naphthol	$Ti(OPr^i)_3Cl$	1:1	i
19	2,2' Biphenol	$Ti(OPr^i)_3Cl$	1:1	i
20	Phenol	$Ti(OPr^i)_3Cl$	1:1	i
21	2-*tert*-butyl-4 methyl plenol	$Ti(OPr^i)_4$	1:1	i
22	2-*tert*-butyl-4 methyl plenol	$Ti(OPr^i)_4$	2:1	i
23	3,3' di-*tert*-butyl-phenol	$Ti(OPr^i)_4$	2:1	i
24	2,4 di-*tert*-butyl phenol	$Ti(OPr^i)_4$	2:1	i
25	5-*tert*-butyl-4 hydroxy-2-methyl phenyl sulphide	$Ti(OC_2H_5)_4$	1:2	i
26	5-*tert*-butyl-4 hydroxy-2-methyl phenyl sulphide	$Ti(OPr^i)_4$	1:2	i
27	5-*tert*-butyl-4 hydroxy-2-methyl phenyl sulphide	$Ti[(CH_3)_2CHCH_2O]_4$	1:2	i
28	5-*tert*-butyl-4 hydroxy-2-methyl phenyl sulphide	$TiCl_4$	1:2	iii

2.4. Ethylene polymerization

Ethylene polymerization was conducted in a 600 mL stirred autoclave (Parr, USA) connected to a model 4850 microprocessor controller shown in Figs .3, 4. Prior to polymerization, the reactor was heated to 150°C under nitrogen for 2h and cooled to ambient temperature. In a typical experiment catalyst and co-catalyst were dissolved in 50 ml of toluene separately. They were carefully charged into the reactor under a nitrogen blanket. Quantities of catalyst and co catalyst were taken to maintain the Al/Ti ratio (see Table under Results & discussion). The reactor temperature was kept at the specified temperature and then pressurized with ethylene to the desired pressure. The reaction was continued for one hour, cooled, the contents carefully degassed and the slurry slowly poured into acidic methanol (5 %, v/v) to precipitate the polymer. The white polyethylene powder was filtered, washed several times with methanol followed by acetone and finally dried under reduced pressure at 70°C for 2 h. All polyethylenes were characterized using different analytical techniques described above.

2.5 References

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Fig. 2.1 Inert atmosphere Glove Box.

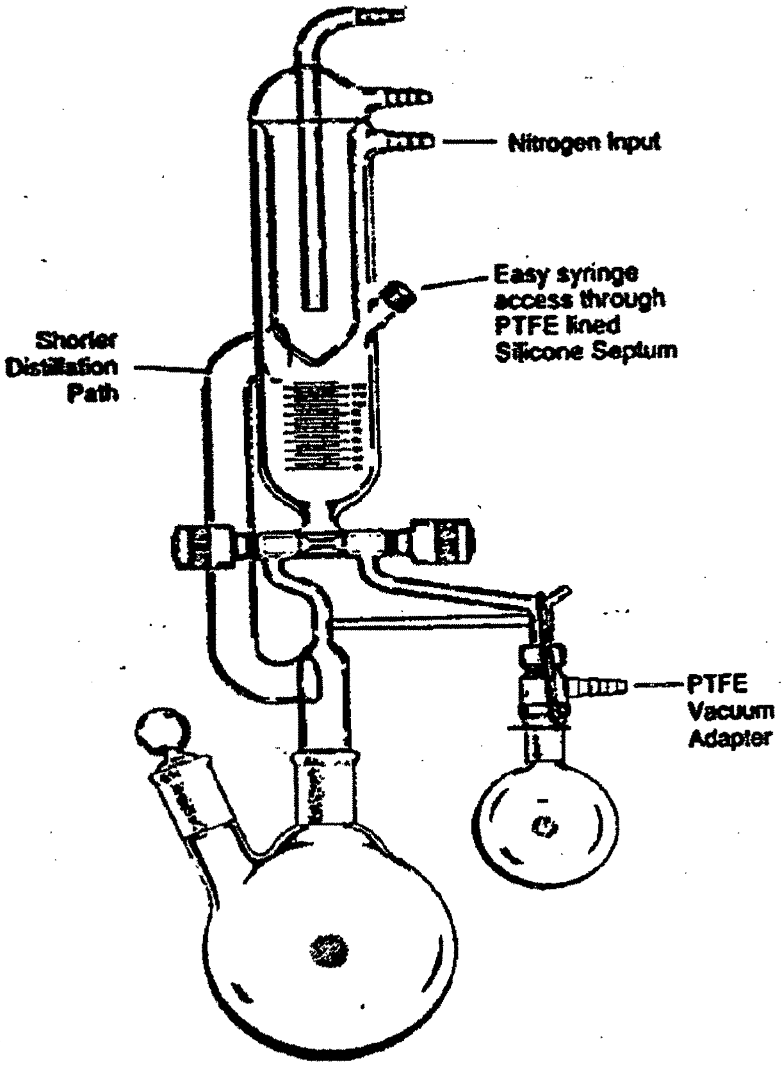

Fig. 2.2 Solvent purification system.

Fig. 2.3 High Pressure Parr Reactor

Fig. 2.4 Assembled High pressure Reactor