

CHAPTER III

EXPERIMENTAL

3.1 Apparatus and instruments

No.	INSTRUMENTS	SOURCES
1.	Aspirator	Eyela, model A-3S
2.	Branauer-Emmett-Teller Meter	Quantachrome
3.	Differential Scanning Calorimeter and Thermal Analyzer	DUPONT, model 910S
4.	Differential Thermal Analyser	Shimadzu, model DT-30
5.	Electronic Shaker	Janke & kunkel, model HS 500
6.	Electronic Grinder	Retsch, model S1
7.	Elemental Analyzer(CHN)	Perkin Elmer, model 24 C
8.	Fourier Transform Infrared Spectrophotometer	Perkin Elmer, model 1760X
9.	Gas Chromatography	Shimadzu, model GC 9 A
10.	High Vacuum Pump	Javac, model JD 60
11.	Hydrogenator with Temperature controller	Parr, model 4541

No.	INSTRUMENTS	SOURCES
12.	Inductively Coupled Plasma Emission Spectrometer	Shimadzu, model ICPS-50
13.	Mechanical Stirrer	Eyela, model MDC-NS
14.	NMR Spectroscopy	BRUKER, model BZH 200/52
15.	Scanning Electron Microscope	JEOL, model JSM-T20
16.	Sonic Filter	Asahi, model A1
17.	Vacuum Oven	Fisher, model 281
18.	Rotary Evaporator	Heidolph, model VV 2000
19.	Mass Spectrometer	JEOL, model JMS-DX-300

3.2 Solvents and reagents

No.	REAGENTS	SOURCES
1.	Acetic acid	Merck , AR
2.	Acetone	Merck , COMMERCIAL
3.	Anthranilic acid	Sigma , AR
4.	Benzene	J.T. BAKER , AR
5.	Benzoyl peroxide	Merck , AR
6.	Boric acid	BDH , AR
7.	2-Bromoethyl benzene	FLUKA AG

No.	REAGENTS	SOURCES
8.	1-Butanol	BDH , AR
9.	Calcium chloride	BDH , LAB
10.	Carbon disulfide	Merck , AR
11.	Chloroform	Merck , AR
12.	Cuprous chloride	FLUKA AG
13.	Cyclohexanol	BDH , AR
14.	Cyclohexanone	FLUKA AG
15.	Cyclohexene	FLUKA AG
16.	Diethyl ether	J.T. BAKER , AR
17.	Divinyl benzene(50% in ethyl vinyl benzene)	FLUKA AG
18.	Ethanol(absolute)	CARLO ERBA , AR
19.	Gelatin powder	BDH , AR
20.	Hydrochloric acid	BDH , AR
21.	Isooctane	CARLO ERBA , AR
22.	4-Methyl-2-pentanol	FLUKA AG, PURUM
23.	Molecular sieve(type 4 A 1/16" pellets)	UNION CARBIDE
24.	Nitric acid	Merck , AR
25.	Paraformaldehyde(extra pure)	Merck , AR
26.	Petroleum spirit(40-60°C)	Merck , AR
27.	Polyvinyl pyrrolidone(MW. 44,000)	BDH , AR
28.	Potassium-tert-butoxide	FLUKA AG

No.	REAGENTS	SOURCES
29.	Potassium thiocyanate	FLUKA AG
30.	Pyridine	CARLO ERBA , AR
31.	Rhodium trichloride	Aldrich , AR
32.	Silver nitrate	Merck , AR
34.	Sodium carbonate anhydrous	FLUKA AG, PURUM
35.	Sodium hydrogen carbonate	RIEDEL-DEHAEN AG
36.	Sodium hydroxide	EKAKEMI, PURISS
37.	Sodium sulfate anhydrous	CARLO ERBA , AR
38.	Styrene	FLUKA AG
39.	Sulfuric acid	J.T. BAKER , AR
40.	Tert-butyl- alcohol	J.T. BAKER , AR
41.	Toluene	BDH, AR
42.	Zinc chloride anhydrous	FLUKA AG, PURISS

3.3 Purification of solvents and reagents

3.3.1 Acetone

Organic impurities in this commercial reagent had been removed by adding 4 g of silver nitrate in 30 ml of water to 1 lit of acetone, followed by 30 ml 1 M sodium hydroxide, shaking for 10 min, filtering, drying with anhydrous calcium sulfate and then fractional distilling. (b.p. 56.2°C)

3.3.2 Benzene

It can be purified by drying with 4X Linde molecular sieve, and fractional distilled. (b.p. 80.1°C)

3.3.3 1-Butanol

This solvent was dried with magnesium sulfate and followed by fractional distillation. (b.p. 117.7°C)

3.3.4 Carbon disulfide

This solvent was dried carefully with calcium chloride and then followed by fractional distillation. (b.p. 46.3°C)

3.3.5 Chloroform

This solvent reacts slowly with oxygen or oxidising agents, when exposed to air and light, giving mainly, COCl_2 , Cl_2 and HCl . Simplest purifications involve drying with CaCl_2 , and distilling. The distilled chloroform should be stored in the dark to avoid photochemical formation of phosgene. (b.p. 61.2°C)

3.3.6 Cyclohexanol

This solvent was dried with sodium carbonate, then fractionally distillation. (b.p. 161.1°C)

3.3.7 Cyclohexanone

This solvent was dried with sodium sulfate, then distilled. (b.p. 155.7°C)

3.3.8 Diethyl ether

This solvent was refluxed with small pieces of sodium metal and benzophenone until the solution was blue colour, followed by fractional distillation. (b.p. 34.6°C)

3.3.9 N,N-Dimethylformamide (DMF)

By using of Linde type 4 A molecular sieves as drying agents, dimethyl formamide was followed by distillation under reduced pressure. (b.p. 153.0°C)

3.3.10 Isooctane (2,2,4-trimethylpentane)

This solvent was fractionally distilled before use. (b.p. 99.2°C)

3.3.11 Methylisobutyl carbinol (4-methyl-2-pentanol)

This solvent was extracted with aqueous sodium bicarbonate, dried with anhydrous magnesium sulfate and distilled (b.p. 131-132°C)

3.3.12 Tert-butyl alcohol

This solvent was dried with anhydrous magnesium sulfate, filtered and fractionally distilled. (b.p. 82.5°C)

3.3.13 Toluene

This solvent was dried with calcium chloride and then by standing with sodium, then fractionally distilled from sodium. (b.p. 110.6°C)

3.4 Purification of monomers and initiator

3.4.1 Benzoyl peroxide

The initiator was dissolved in acetone at room temperature and precipitated by adding two volumes of distilled water. Dried under vacuum. Stored in a dessicator in the dark.

3.4.2 Divinyl benzene (50% in ethylvinyl benzene)

Divinyl benzene was inhibited by 0.1% 4-tert-butylcatechol. This monomer was purified by washing with 10% aqueous sodium hydroxide until inhibitor was essentially removed, then with distilled water until all the base had been removed, and dried with anhydrous sodium sulfate. It was filtered and distilled under reduced pressure in the presence of cuprous chloride, without fractionation, so as to maintain the initial composition of divinyl benzene in ethylvinyl benzene. (b.p. 146-148 °C)

3.4.3 Styrene

Styrene monomer of 99% purity was inhibited with 40-50 ppm p-tert-butylcatechol. This monomer was purified by washing with an equal volume of 10% aqueous solution of sodium hydroxide until liquid became clear, followed by deionized water until the litmus paper showed that all the base had been removed, and dried several hours with anhydrous sodium sulfate. Then it was distilled before use under reduced pressure in the presence of an inhibitor cuprous chloride. (b.p. 142-146 °C)

3.5 Syntheses and characterization

3.5.1 p-Chloromethylstyrene or vinylbenzyl chloride (VBC)

3.5.1.1 Chloromethylation of 2-bromoethyl benzene

In a 1 lit three-necked flask fitted with a reflux condenser, thermometer and hydrogen chloride gas tube, were placed 2-bromoethyl benzene (444 g, 2.4 mol) and 200 ml of carbon disulfide. During the course of reaction, three separate portions of anhydrous zinc chloride (50 g) and paraformaldehyde (60 g) were added to the flask. The reaction mixture was immersed with bubble hydrogen chloride and rigorous stirring for 20 hours at 35-40°C. The reaction mixture was washed with water. The resulting organic layer was washed with diluted sodium carbonate, and again with water. After the extract was dried with anhydrous sodium sulfate, the carbon disulfide was distilled from the product, and the unused 2-bromoethyl benzene was recovered by vacuum distillation at 59-60°C/2 torr.

The resulting mixture of o- and p-(2-bromoethylbenzyl) chloride was gotten by vacuum distillation at 92^o-94^oC/2 Torr. The mixture was dissolved in 200 ml of petroleum benzene and the solution was chilled overnight in a refrigerator. The remaining liquid was removed and the solid was recrystallized about several times from 200 ml of petroleum benzene. The yield was 64 g (46%); mp. 50^o-52^oC.

Spectroscopic data :

IR (KBr pellet) : ν (cm^{-1}) ; 3030, 2970, 1920, 1805, 1690,
1510, 1450, 1420, 1260, 1210,
850, 670, 620.

$^1\text{H-NMR}$ (CDCl_3) : δ (ppm) ; 7.28, 7.18, 4.53, 3.51, 3.12.

$^{13}\text{C-NMR}$ (CDCl_3) : δ (ppm) ; 139.06, 136.06, 129.95, 128.77,
45.89, 38.86, 32.58.

Mass spectrum : (m/e) ; 232(m^+), 197, 153, 139,
117(base peak).

3.5.1.2 Synthesis of vinylbenzyl chloride

Potassium-tert-butoxide (45 g, 0.4 mole) was added to 700 ml of tert-butyl alcohol at 50°C . After all the metal was dissolved, the solution was cooled to the room temperature, and p-(2-bromoethyl benzyl)chloride (93.4 g, 0.4 mole) was added to the solution. The mixture was stirred for two hours at 35°C . Then the mixture was poured into 2 litres of water and extracted with ether. The extract was dried with anhydrous sodium sulfate. The ether was removed under reduced pressure and the rest was distilled in the presence of cuprous chloride to obtain 51.5 g of vinylbenzyl chloride (0.34 mol, 85%); bp. $90^\circ\text{--}94^\circ\text{C}/2$ Torr.

Spectroscopic data :

IR (NaCl cell) : ν (cm^{-1}) ; 3070, 3000, 2940, 2860, 1905,
1820, 1620, 1500, 1255, 1395,
980, 905, 835, 675.

$^1\text{H-NMR}$: (CDCl_3) : δ (ppm) ; 7.46, 7.42, 6.81, 5.94, 5.39,
4.62.

$^{13}\text{C-NMR}$: (CDCl_3) : δ (ppm) ; 136.40, 129.00, 126.67,
114.60, 46.21.

elemental analysis : calcd ; C 70.83%, H 5.94%, Cl 23.23%
found ; C 71.17%, H 5.71%, Cl 23.12%

3.5.2 Crosslinked polymers by suspension polymerization

3.5.2.1 Effects of solvent on the formation of crosslinked polymers with 10% DVB

The suspension polymerizations were carried out in 250 ml resin reaction flask with water-cooled condenser and mechanical stirrer. Flasks were immersed in a thermostated oil bath to maintain constant temperature at 80°C. And then 110 ml of deionized double distillation water was placed in a 250 ml beaker. Gelatin, poly(vinyl pyrrolidone), and boric acid were dissolved in water and pH of the solution was adjusted to about 8 with 50% aqueous sodium hydroxide solution. Only after the pH adjustment did the aqueous mixture become clear. The entire mixture was added carefully to the flask.

A solution of styrene (8.33 g, 80 mmol) , divinyl benzene (2.60 g, 10 mmol) , vinylbenzyl chloride (1.53 g, 10 mmol) and methylisobutyl carbinol(6.23 g) were added slowly to the flask. This was followed by addition of benzoyl peroxide. Nitrogen was swept through the flask for 30 min, and a slight positive pressure of nitrogen was maintained throughout the polymerization. Heating was switched off 10 hours after the introduction of the reaction mixture.

The beads were decanted and then steam distilled to remove the remaining solvent. Then, the polymers were boiled in toluene for 24 hours. Finally, they were dried for 20 hours at 100 °C under vacuum. Sieving was applied to separate the 0.07 to 0.14 mm-diameter fraction.

Suspension polymerization of styrene , divinyl benzene and vinylbenzyl chloride was conducted in the same way as mentioned above except the other solvent was used instead of methylisobutyl carbinol as the same content. These solvents were isooctane, 1-butanol, cyclohexanol, cyclohexanone and toluene. Finally, polymeric supports were measured scanning electron microscope and surface area.

3.5.2.2 Preparation of crosslinked polymers

A typical copolymerization for each crosslinked was prepared. Following the method in 3.5.2.1, the 3% and 20% of crosslinking agent were polymerized with composition shown in Table 3.2. And then the polymeric supports were measured scanning electron microscope, surface area, and thermal analysis measurements.

spectroscopic data :

FT-IR (KBr pellet) : ν (cm^{-1}) ; PX-3 : 3024, 2918, 1601,
1492, 1449, 1267,
698.

PX-10 : 3024, 2921, 1601,
1492, 1450, 1267,
699.

PX-20 : 3024, 2921, 1602,
1491, 1449, 1268,
701.

elemental analysis : PX-3 : C 89.13%, H 7.62%, Cl 3.25%

PX-10 : C 89.60%, H 7.23%, Cl 3.17%

PX-20 : C 88.94%, H 7.91%, Cl 3.15%

Table 3.1 Composition of suspension polymerization at different percent of DVB

Components (g)	Percent of DVB		
	3	10	20
Styrene (g)	9.06	8.33	7.29
Divinyl benzene (g)	0.78	2.60	5.21
Vinylbenzyl chloride (g)	1.53	1.53	1.53
Gelatin (%)	2.20	2.01	1.78
Poly(vinyl pyrrolidone) (%)	0.97	0.88	0.78

3.5.3 Anchoring anthranilic acid to poly(styrene-co-divinyl benzene-co-vinylbenzyl chloride)

3.5.3.1 Effect of solvent

The polymeric support with 10% DVB(0.50 g, 0.3032 mequiv of Cl based on modified volhard method)suspended in 10 ml of acetone was added anthranilic acid (0.30 g, 2.19 mmol). The mixture was vacuum ovened for 24 hours at room temperature. After triturating the beads thoroughly with absolute ethanol, the following procedure was typical. Anthranilic acid was anchored to the beads by stirring the

beads with an excess of anthranilic acid in dimethylformamide and diethyl ether. The polymeric supports with 3 and 20% DVB were anchoring in the same condition with the polymeric support with 10% DVB.

3.5.3.2 Effect of time

The polymeric support with 10% DVB(0.50 g, 0.3032 mequiv of Cl based on modified volhard method)suspended in 10 ml of dimethylformamide was mixed with anthranilic acid (0.30 g , 2.19 mmol). The mixture was vacuum ovened for 18 hours at room temperature, filtered, and washed with absolute ethanol. The following procedure was typical. Anthranilic acid was anchored to the beads by stirring them with an excess of anthranilic acid for 20, 22, 24 and 26 hours. The polymeric supports with 3 and 20% DVB were anchoring in the same condition with the polymeric support with 10% DVB.

3.5.3.3 Effect of temperature

The polymeric support with 10% DVB(0.50 g, 0.3032 mequiv of Cl based on modified volhard method)suspended in 10 ml of dimethylformamide was mixed with anthranilic acid (0.30 g , 2.19 mmol). The mixture was vacuum ovened for 22 hours at room temperature, filtered, and washed with absolute ethanol. The following procedure was typical. Anthranilic acid was anchored to the beads by stirring them with an excess of

anthranilic acid for 50^o, 70^o, 80^o, 90^o and 100^oC. The polymeric supports with 3 and 20% DVB were anchoring in the same condition with the polymeric support with 10% DVB.

3.5.3.4 Preparation of poly(styrene-co-divinyl benzene-co-vinylbenzyl chloride) anchoring anthranilic acid

The polymeric support with 10% DVB(5.00 g , 3.032 mequiv of Cl based on modified volhard method) suspended in 10 ml of dimethylformamide was mixed with anthranilic acid (0.60 g , 4.38 mmol). The mixture was vacuum ovened for 22 hours at 90^oC, filtered, and washed with absolute ethanol. Then, the polymeric ligands were determined thermal analysis. The polymeric supports with 3 and 20% DVB were anchoring with anthranilic acid in the same way.

Spectroscopic data :

FT-IR (KBr pellet) : δ (ppm) ; PL-3 : 3024, 2919, 1686,
1601, 1492, 1450,
698.

PL-10 : 3024, 2920, 1695,
1601, 1492, 1450,
699.

PL-20 : 3025, 2921, 1689,
1602, 1492, 1450,
699.

elemental analysis : PL-3 : C 89.08%, H 7.75%,
N 0.56%, O 2.61%
PL-10 : C 89.24%, H 7.72%,
N 0.54%, O 2.50%
PL-20 : C 88.59%, H 7.73%,
N 0.54%, O 3.14%

3.5.3.5 Chloride analysis by modified volhard method

The polymeric supports were accurately weighed 200 mg in a test tube and heated with pyridine 3 ml for 3 hours at 100°C. Contents were quantitatively transferred into a 125 ml conical flask with 50% acetic acid 30 ml and concentrated nitric acid 5 ml was then added. The mixture was stirred for 30 minutes. Ferric alum indicator 3 drops and standard silver nitrate solution (10 ml, 0.10 N) were then added with stirring. The sides of the flask were washed with minimal amount of distilled water, and toluene 10 ml was added to the flask. The solution was titrated against standard potassium thiocyanate with the mixture being constantly stirred with a magnetic stirrer. The first permanent tinge of red-brown was taken as the end point.

3.5.4 Complexation and reduction of poly(styrene-co-divinyl benzene-co-vinyl benzyl chloride) anchoring anthranilic acid and rhodium(III) chloride.

3.5.4.1 Formation of rhodium(I) polymer-bound catalysts

A mixture of anthranilic acid anchored beads with 10% DVB (4.00 g , 0.2570 mmol of N) was stirred for 24 hours with rhodium trichloride (0.10 g , 0.38 mmol) in sodium ethoxide solution and then the mixture was vacuum ovened overnight for completely complexation of over all beads. After filtration, the beads were washed with 200 ml of absolute ethanol, .suspended in 5 ml of absolute ethanol and treated with sodium borohydride (0.1 g). After 0.5 hour the beads were washed with ethanol and air dried.

3.5.4.2 Determination of rhodium incorporation

3.5.4.2.1 Preparation of standard calibration curve

In a typical procedure , rhodium trichloride (3.5 mg, 0.0167 mmol) was weighed accurately and dissolved with 50% potassium hydroxide solution 2 ml. After that it was transferred to a volumetric flask to make a volume of 100 ml. The solution were 0.8606 ppm and 1.7212 ppm of rhodium

it was transferred to a volumetric flask to make a volume of 100 ml. The solutions were 0.8606 ppm and 1.7212 ppm of rhodium were prepared from the original solution by dilution. These solutions were then used to prepare a calibration curve by plotting absorbance with concentration at 233.48 nm with ICPS techniques.

3.5.4.2.2 Spectrophotometric determination of rhodium incorporation

Rhodium polymer-bound catalysts with 3, 10 and 20 % DVB were weighed accurately about 0.1 g and placed in three combustion boats. Then, they were introduced to the furnace at 500°C. After that they were digested with aqua regia until they dissolved and neutralized with 50% potassium hydroxide solution until they were the basic solution. Finally, they were introduced to the volumetric flasks to make volume to 25 ml with double distillation water. These solutions were determined rhodium content by ICPS techniques.

3.5.5 Preliminary study of catalytic cyclohexene hydrogenation using rhodium(I) polymer-bound catalysts

The substrate (40 ml, 0.4 mol), cyclohexene, and Rh(I) polymer-bound catalysts with 3% DVB were introduced to hydrogenation reactor and then the cover with thermocouple, inlet hydrogen gas way, and outlet hydrogen gas way were

reactor to pressurize to 60 psig. The reactor was started with stirring the mixture. Samples were withdrawn from the reaction mixture at regular time intervals and were analyzed by gas-liquid chromatography. Until the reaction was completed, the stirring was stopped.

In a typical procedure, Rh(I) polymer-bound catalysts with 10 and 20% DVB with a same rhodium content were used. The catalyst was removed by filtration and washed by absolute ethanol solution until the solution became clear. The catalysts were checked the rhodium leaching content by ICPS techniques.

Table 3.2 The weight of polymeric catalysts used in cyclohexene hydrogenation

Polymeric catalysts	weight (g)
PC-3	1.23
PC-10	1.55
PC-20	1.72

3.5.6 Characterization of polymer-bound catalysts

3.5.6.1 Fourier-transform Infrared spectroscopy

FT-IR spectrometer was used to obtain fourier-tranform infrared spectra. The monomers were determined neat and the polymers as KBr pellets. The polymers were grinded and dried in vacuum oven to make sure that the solvent were removed completely.

3.5.6.2 ^1H and ^{13}C Nuclear Magnetic Resonance spectroscopy

Nuclear magnetic resonance spectra were obtained on 200 MHz . Deuterated chloroform(CDCl_3) was used as the solvent and tetramethylsilane(TMS) was used as the internal standard. For ^1H -NMR spectra , values were reported in ppm from TMS. Abbreviations were used: s=singlet, d=doublet, t=triplet, q=quartet, m=multiplet.

3.5.6.3 Elemental analysis (C, H and N)

The carbon, hydrogen and nitrogen content were measured by CHN elemental analyzer. The polymers were weighed by ultramicrobalance and then they were placed in sample holder. They were oxidized in combustion zone under pure oxygen gas atmosphere. The carbon , hydrogen and nitrogen were

oxidized to carbon dioxide, vapor and nitrogen gas, respectively. All of gases were passed to gas control zone where the pressure, temperature and volume were determined. Each gas was separated and detected quantitatively by thermal conductivity detector in separation zone and detector zone, respectively. The percentage of each gas was calculated as shown in appendix II.

3.5.6.4 Gas-liquid chromatography

About 0.3 ml of mixture from cyclohexene hydrogenation was drawn out of the bomb reactor and then it was made to 1% of mixture in hexane. 0.6 microlitre of this solution was injected to gas-liquid chromatography with a flame ionization detector. Nitrogen gas was used as carrier gas with flowrate 43 ml/min. A capillary column (25 m * 0.2 mm) filled with OV1-01 was used. The temperature of the injection port was 150°C and the temperature program was starting from 50°C for 3 min and then the rate 10°C/min was used to raise the temperature to 100°C and stand for 1 min. From this temperature to 150°C was increased with the rate 5 °C/min and stand for 10 min before cooling down.

3.5.6.5 Texture determination

3.5.6.5.1 Scanning Electron Microscope (SEM)

For morphology studies, bead size and shape were determined with a scanning electron microscope. About 5 beads were selected at random and measured. The overall and half sectioned beads were mounted on a copper stud and then coated under vacuum with a thin layer of gold.

3.5.6.5.2 Surface area measurement

The surface area was obtained from nitrogen adsorption measurements following the BET method. Polymer were accurately weighed and filled in the BET standard glass cell. The gas mixture of helium and nitrogen gas were passed into this system with flowrate $39 \text{ cm}^3/\text{min}$. And then polymers were degassed at 100°C for two hours to get rid of moisture and other impurities which might remain in the pores of these polymers, they were then cooled to room temperature. Then, these polymers were chilled in liquid nitrogen. The amount of nitrogen desorped was measured by using TCD detector. The 1 cm^3 of nitrogen gas was injected behind the detector. Standard nitrogen peak and polymer peak were calculated following the equation below.

$$S_B = SV_m$$

when $V_m = V(1-P/P_0)$

$$V = [(S_2/S_1)(273.15/T)]/w$$

S_B surface area of catalyst sample, m^2/g

S surface area of nitrogen gas, m^2/cc

V_m amount of adsorption to cover the surface, cm^3 at
NTP/g of catalyst sample

V amount of adsorption at the equilibrium, cm^3 at
NTP/g of catalyst sample

P equilibrium vapour pressure of nitrogen gas

P_0 saturation vapour pressure of nitrogen gas

w weight of catalyst sample

3.5.6.5.3 Total pore volume measurement

The total pore volume is derived from the amount of vapor adsorbed at a relative pressure close to unity, by assuming that the pores are then filled with liquid adsorbate. The volume of nitrogen adsorbed (V_{ads}) can be converted to the volume of liquid nitrogen (V_{liq}) contained in the pores using following equation.

$$V_{liq} = \frac{P_a V_{ads} V_m}{RT}$$

when P_a and T are ambient pressure and temperature, respectively and V_m is the molar volume of the liquid adsorbate ($34.7 \text{ cm}^3/\text{mol}$ for nitrogen).

3.5.6.6 Thermal analysis

3.5.6.6.1 Differential scanning calorimetry

Diferential Scanning Calorimetric (DSC) measurement were conducted on 10 mg specimens at a heating / cooling rate of 10°C/min from ambient temperature to 500°C under a static atmosphere in nitrogen atmosphere. The melting point and heat of fusion were obtained from the peak temperature and peak area of the endothermic peak, respectively. The relative thermal stability of the experiment resins was quantitatively estimated by comparing temperatures for a particular degree of weight loss.

3.5.6.6.2 Differential thermal analysis

Differential thermal analysis (DTA) measurements were conducted on 10 mg on a opened cell at a heating rate of 10°C/min from room temperature to 200°C under nitrogen atmosphere with a rate of 30 ml/min. The sensitivity was 25 volt and chart speed 2.5 mm/min.