



*Chapter - 2*  
**Experimental**

## 2.0 Experimental

### 2.1 Materials :-

Dimethyl formamide (DMF), methanol, hexamethyl phosphoramide (HMPA), *m*-cresol, tetrahydrofuron (THF), dichloromethane (DCM), chloroform, tetrachloroethane (TCE), ethanol, triphenyl phosphite, benzene, hexane, pyridine, lithium chloride, N – methyl – 2 – pyrrolidone (NMP) and N – N – dimethyl acetamide (DMAc) were purified before use by following standard procedures as briefly given below.

- 1) Benzene was dried over calcium chloride, distilled and then refluxed over sodium for 6 h, distilled and stored over Linde type 4A molecular sieves.
- 2) Hexane (60 – 80 °C fraction from petroleum) was refluxed over phosphorous pentaoxide for 4 h, distilled and stored over sodium wire.
- 3) Pyridine was refluxed with solid potassium hydroxide pellets, fractionally distilled and stored over Linde type 4 A molecular sieves.
- 4) Lithium chloride was dried under vacuum at 150°C for 6 h.
- 5) N-methyl-2-pyrrolidone (NMP) was dried by azeotropic removal of water with benzene for 6 h, distilled under reduced pressure and stored over Linde type 4A molecular sieves.
- 6) N-N dimethyl acetamide (DMAc) was refluxed over barium oxide for 4 h, the liquid was decanted a separate round bottom flask and distilled at reduced pressure over calcium hydride and stored over Linde type 4 A molecular sieves.

The various aromatic diamines were purified prior to use by methods given below *p*-phenylene diamines (*p*-PDA) was purified by sublimation under reduced pressure, *m*-phenylene diamines (*m*-PDA) was purified by vacuum distillation. 4,4'- Diaminodiphenyl ether (ODA), 4,4'- diamino diphenyl sulfone (SDA) were recrystallised prior to use from alcohol. 1,5- Diamino naphthalene (NDA) was purified by sublimation under vacuum (at 180 °C at < 1mm Hg prior to use). 2,5 – Bis (4-aminophenyl) 3, 4-diphenyl thiophene (TPTPDA) was

synthesized in the laboratory as reported previously by us <sup>111</sup> and purified by recrystallisation from toluene.

Trimellitic anhydride was obtained by sublimation of trimellitic acid under reduced pressure, and the sublimate was washed with dry hexane, under inert atmosphere.

## **2.2 Synthesis of monomer (IV) : -**

### **2.2.1) Tetraphenyl thiophene (I) : -**

In a 500 mL three neck round bottom flask equipped with a reflux condenser and a stirrer, a mixture of 126.69 g (115.1 mL, 1mol) benzyl chloride and 19.2 g (0.6 mol) powdered sulphur was stirred under reflux temperature until the reaction temperature reached to 240°C (required about 15 h.). Then the reaction mixture was refluxed for 3 h at 240°C and the mixture was allowed to cool to 60 °C, and 100 mL ethanol was added. The resulting solid was filtered, washed with methanol. The crude tetraphenyl thiophene was recrystallised from dichloromethane – methanol system to give white needles.

Yield :- 39.6 g (51%),

M.P. :- 184 - 185°C (Lit. M. P. 184 - 185°C),

IR (KBr) :- 3060 (aromatic C – H stretch), 1595 (aromatic C=C) and 1435 cm<sup>-1</sup> (thiophene).

### **2.2.2) 2,5 – Bis (4 – nitrophenyl) –3, 4 – diphenyl thiophene (II) : -**

In a 1000 mL three neck round bottom flask equipped with a reflux condenser and a magnetic stirrer, a mixture of 30 g (0.0774 mol) (I) in 600 mL glacial acetic acid was stirred at 100°C. A mixture of 60 g (43.38 mL) concentrated nitric acid (density 1.4 g/cm<sup>3</sup>) and 60 mL glacial acetic acid was added dropwise through dropping funnel over a period of 1 h. After complete addition of acid mixture, the reaction mixture was stirred at 100°C for an

additional 30 minute. The clear yellow solution was allowed to cool to give crystalline dinitrotetraphenyl thiophene. It was filtered and was recrystallised from glacial acetic acid to afford bright yellow needles (II). The crystals were filtered and dried under vacuum at 100°C for 6 h.

Yield :- 18.3 g (50%),

M.P. :- 216 - 217°C (Lit 217 - 218°C),

IR (KBr) :- 1510 and 1340  $\text{cm}^{-1}$  ( $\text{NO}_2$ ).

### **2.2.3) 2,5 – Bis (4-aminophenyl) –3,4 – diphenyl thiophene (III) :-**

In a 500 mL three neck round bottom flask equipped with mechanical stirrer, reflux condenser and thermowell, a mixture of 10.04 g (0.021 mol) (II) and 100 mL glacial acetic was stirred. To this 50 g (0.221 mol) stannous chloride dihydrate in concentrated hydrochloric acid was added all at once. The reaction solution was heated for 4 h at 100°C then the cooled reaction mixture was slowly added to 270 mL 40% sodium hydroxide solution, so as to get free diamine. After stirring the mixture for 30 minute; it was poured into ice water. The precipitate was filtered, dried and extracted with hot toluene. Concentration of toluene extracts gave pale cream coloured powder, which was recrystallised twice from toluene to give small white needles of ( III ).

Yield :- 4.64 g (53%),

M.P. :- 273 - 274°C (Lit. M.P. - 273°C),

IR (KBr) :- 3420 and 3340  $\text{cm}^{-1}$  ( -  $\text{NH}_2$ ).

### **2.2.4) Trimellitic anhydride :-**

It was obtained by heating trimellitic acid under high vacuum to yield sublimate of trimellitic anhydride which was washed with dry hexane and dried under nitrogen.

M.P.:- 161 – 162°C (Lit. M.P. 161 – 163.5°C).

### 2.2.5) 2,5 – Bis(4-trimellitimidophenyl)–3,4-diphenyl thiophene (IV) :-

In a 250 mL three neck round bottom flask equipped with Dean Stark assembly, magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 4.18 g (0.01 mol) ( III ) in 80 mL N-N-dimethylacetamide (DMAc), stirred at 0°C and added 3.84 g (0.02 mol) solid trimellitic anhydride in small lots over 10 minutes period. The temperature was maintained at 0°C for 1 h and for 4 h. at room temperature. Then 50 mL dry toluene was added, and mixture was refluxed until 0.36 g of water was distilled off azeotropically. Heating was continued to distill off the residual toluene, after cooling to room temperature, the yellow precipitate of ( IV ) was isolated by filtration and washed with methanol.

Yield :- 6.20g (80.93%),

M.P. :- 345°C (by DSC) [Lit. M.P. 346-347°C],<sup>110</sup>

IR(KBr) :- 3436 cm<sup>-1</sup> (-OH), 1778 cm<sup>-1</sup> asymmetrical stretching of imide carbonyl, 1713,1721,1727 cm<sup>-1</sup> acid carbonyl, 729 cm<sup>-1</sup> imide ring deformation.

Elemental analysis :- For C<sub>46</sub>H<sub>26</sub>N<sub>2</sub>O<sub>8</sub>S :

Calcd. :- C, 72.06; H, 3.39; N, 3.65; S, 4.17 %;

Found :- C, 71.34; H, 3.70; N, 3.63; S, 4.14 %.

### 2.3 Synthesis of poly (amide-imide)s :-

Number of poly(amide-imide)s and copoly(amide-imide)s were prepared following Yamazaki's phosphorylation method, and using (IV) as the building block. Typical polymerization procedure is described below:

In a 100 mL three neck round bottom flask equipped with reflux condenser magnetic stirrer, calcium chloride guard tube and nitrogen gas inlet were placed 0.766 g (1 mmol) (IV), 0.200 g ((1 mmol) 4,4' diaminodiphenyl ether (ODA), 0.200 g lithium chloride [8 wt % based on solvent N-methyl

pyrrolidone (NMP) and pyridine mixture] and 0.744 g (0.63 mL, 2.4 mmol) triphenyl phosphite (TPP), 0.5 mL pyridine and 2 mL NMP. The mixture was stirred well, temperature was slowly raised to 100 °C and the mixture maintained at 100 °C for 3 h. After cooling, the resulting viscous mixture was poured into rapidly stirred 200 mL methanol. The precipitated polymer (P-1) was filtered, washed with methanol and air dried. The polymer was purified by dissolving in N, N-dimethyl acetamide (DMAc) and reprecipitating by methanol. It was filtered, washed with methanol and dried under vacuum at 100 °C for 8 h. The yield was 99% and the reduced viscosity of polymer in DMAc was 2.01 dL/g. All other poly (amide-imide)s [P-2 to P-5] were similarly prepared.

Further, two series of copoly (amide-imide)s were synthesized utilizing above procedure, where in a mixtures of different mol % proportions of (IV) and oxybis-benzoic acid were polycondensed with oxydianiline (CPO-1 to CPO-4 and P-1) or 4,4'-diaminodiphenyl sulphone (CPS-1 to CPS – 4 and P-5).

#### **2.4.0 Measurements : -**

##### **2.4.1 Physical constant : -**

Melting points were taken from Tempo melting point apparatus or from a Rigaku TG – DSC at heating rate of 10°C/ minute in nitrogen.

##### **2.4.2 Infrared Spectrum : -**

Infrared measurements were performed on a Perkin-Elmer infrared spectrophotometer – 883 using KBr pellet.

##### **2.4.3 Nuclear Magnetic Resonance Spectra : -**

The NMR spectra were recorded on Varian 80 spectrometer using tetramethyl silane as an internal reference in deuterated solvents such as deuteriochloroform or hexadeutero dimethyl sulphoxide.

#### **2.4.4 Mass Spectra : -**

High resolution mass spectra were obtained on I IMS 30 double beam mass spectrometer.

#### **2.4.5 Elemental analysis : -**

Elemental analysis was performed with a Perkin-Elmer model 2400 C, H, N, S analyzer.

#### **2.4.6 Reduced Viscosity : -**

Inherent viscosities were measured in DMAc containing lithium chloride at 30°C using an Ubbelohde suspended level dilution viscometer, at 0.5% (w/v) concentration of polymer. Following equation was employed for the determination of reduced viscosity.

$$\eta_{red} = \frac{(t/t_0)-1}{C}$$

Where as  $t$  and  $t_0$  are flow times for polymer solution and solvent respectively and  $C$  is the concentration of polymer solution in g/100 mL i.e. g/dL.

#### **2.4.7 Solubility : -**

Solubilities were determined at a 1% (w/w) concentration in various solvents at room temperature or on warming, if needed.

#### **2.4.8 TGA, DSC, DTA : -**

Thermal stability and glass transition temperature were determined on a Rigaku Thermoflex – 8800 at a heating rate of 10°C/min. under nitrogen. The Tg

was taken as the mid point of the change in the slope of the base line. Thermal stability was measured by weight loss of the polymer samples from 25 to 800°C.

#### **2.4.9 X-ray diffraction : -**

Wide angle x-ray diffractograms were obtained on Philips X-ray unit (Philips generator, PW-1730) and a nickel filtered  $\text{CuK}_\alpha$  radiations.