CHAPTER-II

EXPERIMENTAL

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2.1 Materials :

Phenol and phenolphthalein (LOBA); m-toluidine and p-toluidine (MCC), Dichloromethane, n-Hexane, Triethylamine and methanol (S.d.Fine Chem. Ltd. Bombay)- all were purified by using standard procedures.

2.2 Synthesis of Monomer

2.2.1 Synthesis of 1-H Isoindole-1-One-2,3 dihydro -3,3 bis (4-hydroxy phenyl) -2-(3-methyl phenyl),i.e. phenolphthalein [3-methyl anilide] (3-PMA)

The synthesis of 1-H Isoindole-1-One-2,3, dihydro-3,3 bis-(4-hydroxy phenyl)- 2-(3-methyl phenyl) i.e. phenolphthalein-[3-methyl anilide] (3-PMA) involved two steps viz.

A] Synthesis of m-toluidine hydrochloride and

B] Synthesis of 3-PMA by reaction of phenolphthalein with m-toluidine hydrochloride.

A] Synthesis of m-toluidine hydrochloride

In a 500 ml three neck round bottom flask equipped with a magnetic needle, a gas inlet, a thermowell and an air condenser with $CaCl_2$ guard tube, m-toluidine 10 gm (0.09 mole) and diethyl ether 200ml were placed. The flask was cooled to 0°C and while stirring dry HCl gas was passed for two hours to precipitate m-toluidine hydrochloride as a white crystalline solid. 100ml ether was then added and dry nitrogen gas was passed to remove excess

of HCl gas from the reaction mixture. Complete removal of HCl gas was checked and m-toluidine-hydrochloride was quickely filtered. It was washed with dry ether (3 x 100ml) to remove unreacted m-toluidine, if any. Residual product was dried at 25°c/ 1 mm Hg for five hours.

Yield - 12.9 gm (96.2%)

M.P. - 210°C.(d)

B) Synthesis of 3-PMA

In a 250 ml three neck round bottom flask fitted with a gas inlet, a thermowell and an air condenser with $CaCl_2$ guard tube, phenolphthalein 10gm (0.03 mole), m-toluidine-hydrochloride 11.08 gm. (0.07 mole) and distilled m-toluidine 30 gm (0.28 mole) were placed. A slow stream of nitrogen gas was contineously passed through the flask and mixture was heated to reflux temperature of 200°C for 6 hours. Then allowed to cool to 125°C and reaction mixture was poured into ice-cold 75 ml conc. hydrochloric acid. Pale-green precipitate of 3-PMA was stirred for 45 minutes, filtered, washed with water (5x200 ml) till free from acid and dried. Crude 3-PMA was purified by washing with dichloromethane and then dissolving 10 gm in 10% NaOH solution (125 ml) and filtered. Filtrate was cooled in an ice bath and acidified with 1:1 HCl to precipitate white crystalline-3-PMA, filtered, washed with ice-cold water till free from acid and dried. It was further recrystallised from aq. methanol by charcoal treatment to yield white crystalline 3-PMA.

Yield - 8.5 gm (63%)

M.P. - 288°C.

2.2.2 Synthesis of 1-H Isoindole-1-One-2,3-dihydro-3,3 bis (4- hydroxyphenyl)-2-(4-methyl phenyl) i.e. phenolphthalein-[4-methyl anilide] (4-PMA)

The synthesis of 1-H Isoindole -1-one-2,3 dihydro-3,3 bis-(4-hydroxy phenyl)-2-(4-methyl phenyl) i.e. 4-PMA was performed following the procedure as described for 3-PMA above in two steps from p-toluidine.

Yield of p-toluidine hydrochloride- 12.9 gm (96.2%), M.P. - 235°C(d); Yield of 4-PMA- 8 gm (62.5%) M.P. - 270°C.

2.3 Preparation of Terephthaloyl Chloride

In a 100 ml round bottom flask equipped with a reflux condenser with $CaCl_2$ guard tube, terephthalic acid, 20gm (0.12 mole) and dry pyridine 0.6 ml were placed. Thionyl chloride 100 gm (0.77 mole) was introduced cautiously to it and reaction mixture was refluxed for 12 hours. The reaction mixture was cooled and excess of thionyl chloride was removed by distillation. Last traces of thionyl chloride were removed by adding to flask 30 ml dry benzene and redistilling the same. The residue was distilled at 115°C/3 mm Hg using a short distillation path. The distilled product was crystallised from dry hexane (1gm in 7ml solvent)

Yield - 18 gm (72.7%), M.P. - 79°C.

2.4 Synthesis of Poly (phenolphthalein Terephthalate) i.e. PTPC, By Interfacial Polycondensation Method

Phenolphthalein 0.636 gm (2 m mole), NaOH pellets 0.160 gm (4m mole) and phase transfer catalyst cetyltrimethyl ammonium bromide 0.1 gm dissolved in 25ml of distilled water were placed in a stainless steel container of the blender mixer. With rapid stirring solution of terephthaloyl chloride 0.406 gm (2 m mole) in 6ml dry distilled dichloromethane was introduced all at once into the blender mixer. The stirring was continued for additional five minutes and hexane (50 ml) was added to precipitate the polymer PTPC. The polymer, filtered, washed with water (6 x 150 ml) by stirring vigorously in beaker. Polymer was filtered and dried under vacuum at 80°C/1 mm Hg for 20 hours. Yield : 0.60 gm, reduced viscosity 0.67 dL/g [in sym-tetra chloroethane-phenol, 40/60 w/w].

2.5 Interfacial Polymerisation of 3/4-PMA i.e. Polyesters NMTC/NPTC

3-PMA 0.407 gm, (1m mole), NaOH pellets 0.080 gm, (2 m mole) and phase transfer catalyst cetyltrimethyl ammonium bromide 0.05gm were dissolved in 12 ml distilled water in a stainless steel container of the high speed blender mixer. With the rapid stirring solution of terephthaloyl chloride 0.203 gm (1m mole) dissolved in 5ml dry distilled dichloromethane was introduced all at once. The stirring was continued for five minutes and hexane (50ml) was added to it to precipitate the polymer. The polyester was filtered, washed with water (6 x 150 ml) by stirring vigorously and filtered. Polyester NMTC was dried under vacuum at 100°C/1mm Hg for 10 hours. Yield 0.57g,

reduced viscosity 0.388 dL/g (in sym-tetrachloroethane-phenol; 40/60 w/w).

By similar procedures polymerisation of 4-PMA was performed to yield the correspondng polyester, NPTC 0.580 gm, reduced viscosity 0.309 dL/g [in sym-tetrachloroethane-phenol; 40/60 w/w].

2.6 Synthesis Of Poly (Phenolphthalein Terephthalate) By Low-Temperature Solution Polymerisation i.e. Polyester PTPC

A 100 ml three neck round bottom flask equipped with a magnetic bar, $CaCl_2$ guard tube, a gas inlet and a dropping funnel was flame dried and cooled under stream of dry nitrogen gas. Phenolphthalein 0.318 gm (1 m mole), dry distilled dichloromethane,(5ml) dry distilled triethylamine (0.4 ml) were placed and cooled to 0°C. A solution of terephthaloyl chloride (TPC) 0.203 gm (1m mole) in dichloromethane (5 ml) was added dropwise over a period of 20 minutes. With the help of additional dichloromethane (3 ml) acid chloride, washed into the reaction flask. The reaction mixture was stirred at 0°C for 30 minutes when it became viscous. The stirring was continued at 25°C for 1 hour, and solution diluted with (5 ml) dichloromethane and the dilute mixture was poured slowly into 50 ml hexane to precipitate the white polymer, PTPC, which was collected by filtration. Polymer was washed with water (6 x 100ml) vigorously in the beaker, filtered, and dried at 80°c/1mm Hg for 20 hours. Yield 0.427gm (95.1%) and reduced viscosity 0.685 dL/g (in sym - tetra chloroethane-phenol, 40/60 w/w).

2.7 Low-Temperature Solution Polymerisation Of 3/4 -PMA i.e.Polyesters NMTC/NPTC

A 100 ml three neck round bottom flask equipped with a magnetic needle, $CaCl_2$ guard tube, a gas inlet and a dropping funnel was flame dried and cooled under a stream of dry nitrogen gas. 3-PMA, 0.814 gm (2m mole), dry distilled dichloromethane (6ml) and dry distilled triethylamine 0.7ml (7 m mole) were placed in the flask and cooled to 0°C by ice-salt bath.Terephthaloyl chloride (TPC) 0.406gm (2m mole) in dichloromethane, (6ml) was added dropwise over a period of 30 minutes. Fresh dichloromethane (5ml) was used to wash down the acid chloride from dropping funnel, if any.

The reaction mixture was stirred at 0°C for 30 minutes when it became syrupy. The mixture was then stirred at 25°C for 1 hour. It was diluted with solvent (5ml) and the dilute solution was poured slowly into hexane (100ml) to precipitate the white polyester NMTC which was collected by filtration. It was washed with water (10 x 150ml) by stirring vigorously in the beaker, filtered, and dried at 110°c/1mm Hg for 12 hours. Yield - 1.04g (96.8%) and reduced viscosity 0.834 dL/g (in sym - tetrachloroethane-phenol, 40/60 w/w).

Following the similar procedure, polymerisation of 4-PMA with TPC was performed, to yield the corresponding polyester NPTC 1.06gm (98.7%) with reduced viscosity of 0.739 dL/g (in sym-tetrachloroethane-phenol, 40/60 w/w).

2.8 Synthesis Of Copolyesters Of 3/4-PMA

Using low-temperature solution polymerisation method two series IA-IIIA and IB-IIIB of copolyesters from TPC and various mole proportions of (phenolphthalein + 3-PMA) or (phenolphthalein + 4-PMA) were prepared. Copolyesters with reduced viscosity in the range of 0.368 to 0.580 dL/g, and 95-98% yields were obtained.

2.9 Measurements

Reduced Viscosty :

Viscosity measurements were made with 0.5% (w/v) solutions of polymer in sym. tetrachloroethane-phenol mixture (40:60 w/w) at 25° C using a suspended type Ubbelohde viscometer. The following equation was employed for the determination of reduced viscosity.

$$\eta_{red} = \frac{\frac{t}{to} - 1}{c}$$

where - t and to are flow time for polymer solution and solvent respectively and c is the concentration, in gm/100ml, of the polymer solution.

Solubility :

The solubility of polyesters and copolyesters was determined at 3% concentration in various solvents at room temperature/or on warming, if needed.

Elemental Analysis

Elemental analyses were run in a Perkin-Elmer Model 2400, C, H, N analyser.

Infra-red Spectra

The transmission IR spectra of samples were recorded on a

Perkin-Elmer 883IR spectrophotometer by KBr pellet technique.

Nuclear Magnetic Resonance Spectra

Proton NMR spectra were recorded on Varian-80A spectrometer at room temperature in DMSO d_6 or $CDCl_3$ with tetramethyl-silane (TMS) as an internal standard.

Mass Spectrum

The mass spectra were recorded on IIMS 30, double beam mass spectrometer.

X-ray Diffractograms

The x-ray diffractograms of polymers were obtained with Phillips x-ray unit (Phillips Generator PW-1730) and Nickel filtered CuK_{α} radiations.