

CHAPTER II

EXPERIMENTAL

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2.1 MATERIALS

- 1] Commercially available isophthalic and terephthalic acid were procured and used as received.
- 2] Thionyl chloride was distilled before use.
- 3] Pyromellitic dianhydride was purified by recrystallisation from acetic anhydride, mp 286°C and it was sublimed prior to use.
- 4] Lithium chloride (anhydrous) Loba-Chemie, Bombay, was dried under vacuum at 120° for 4-6 hours.
- 5] Distilled cashew nut shell liquid i.e. cardanol was obtained from M/s Mercury Resins and Polymers Pvt.Ltd., Hyderabad.
- 6] All solvents viz. Pyridine, N-methyl-2 pyrrolidone, m-cresol, p-cresol, n-hexane etc. were purified in the usual manner by distillation and were stored over appropriate drying agents.
- 7] 4-Amino -3-pentadecyl phenol was synthesized as in scheme 3 and it was purified by recrystallisation from ethanol.

2.2 INSTRUMENTAL

1. Melting points were determined in capillary tubes employing an electric heated apparatus and are uncorrected.
2. Infrared spectra were taken on a Perkin-Elmer 883 spectrophotometer, using the potassium bromide pellet technique or Nujol mull technique.
3. The H-1-NMR spectra were recorded in CDCl₃ on FT-80A NMR spectrometer using TMS as internal standard.

4. C-13 NMR (1H decoupled and DEPT) were recorded on AC-200 (super condu.) NMR spectrometer using DMSO-d6 solvent and chemical shifts are expressed in ppm from TMS. Elemental analysis of compound is carried out by microanalytical procedure for carbon, hydrogen and nitrogen.

5. Inherent viscosity of polymers was measured at 0.5% concentration in NMP at 30°C using modified Ubbelohde viscometer.

The following equation was employed for the determination of inherent viscosity.

$$\eta_{inh} = \frac{2.303 \times 10^5 t/t_0}{C}$$

Where, t and t₀ are flow time for polymer solution and solvent respectively and C is the concentration in gm/100ml of the polymer solution.

6. The mass spectra were run on IIMS-30 double beam mass spectrometer.

2.3 IMIDE CONTAINING BISPHENOL (II) SYNTHESIS

Cashewnutshell liquid (CNSL)

The refined cashewnutshell liquid was used throughout the work of present investigation.

Specifications for cashewnutshell liquid (CNSL) of export variety (Kerala State Govt., India) are :

- | | |
|--------------------------------|--------------|
| 1) Specific gravity | 0.985 |
| 2) Viscosity | 434.1 cp. |
| 3) Moisture | 1.17% (max.) |
| 4) Matter insoluble in toluene | 0.20% (max.) |

5) Volatiles	5.2% (max.)
6) Iodine value	234.0
7) Polymerisation test	
a) gel time	10 min. and 6 sec.
b) Oven test (viscosity)	10.21 cp.

2.3.1 3-Pentadecenyl phenol (Anacardol)

Raw commercial cashewnutshell liquid (heat extracted) (900g) was distilled from a 2 litre round bottom flask, under vacuum. The flask was heated slowly till the initial frothing subsided and distillate was collected between 190-200/2-4 mm. Yield 410 g. b.p. 195-200°C/2 mm (redistilled).

Analysis Found C 83.80, H 10.56%

$C_{21}H_{32}O$ requires C 83.94, H 10.76%

2.3.2 3-Pentadecyl phenol (Tetrahydro anacardol)

i) Cardanol (anacardol) (300g) dissolved in 600 ml ethanol was hydrogenated at 70°C in a 2 litre Parr autoclave under 600 psi pressure of hydrogen in the presence of 3-5 g of Raney nickel catalyst, which was prepared according to the W-2 method. When no more absorption was noticed the reaction was stopped, the product filtered and solvent distilled out. Recrystallization from pet. ether (40-60°C) gave white waxy solid 3-pentadecylphenol. Yield 270 g, m.p. 50-51°C

ii) Cardanol (250 g) was hydrogenated with 2% concentration of raney nickel catalyst (based on the cardanol) at 150°C and 150 psi hydrogen pressure in a Parr autoclave. The degree of hydrogenation was judged from samples taken at 15 min. intervals and monitored by TLC technique. Hydrogenation was continued till a single spot on the plate, corresponding to that for 3-pentade-

cylphenol was obtained. There was reduction in the period of hydrogenation to get the desired product (4h.)

Solution was filtered to remove catalyst and solvent distilled at atmospheric pressure. Distillation of residue under reduced pressure gave a white crystalline product. Yield 220 g, b.p. 215-220°C/3-4 mm. m.p. 51°C.

2.3.3 4-Nitro-3-pentadecylphenol

3-Pentadecylphenol was nitrated with fuming nitric acid (sp.gr. 1.5) below 10°C, in chloroform.

3-Pentadecylphenol (20 g), dissolved in 75 ml of chloroform was taken in a 250 ml beaker. 5.3 g (1.2 mole) of fuming nitric acid (sp.gr. 1.5) was added to it dropwise with stirring and cooling in an ice-bath. The temperature was maintained at 5-10°C. during the 10 minutes of addition of the acid and the solution was stirred for another 20 minutes at 10°C. The reaction mixture was poured into water, solvent removed in vacuo and the residue solidified on cooling in freez. After filtration and drying 23g of red-orange solid obtained. The crude solid mixture of monoⁿnitro isomers of 3-penadecylphenol was dissolved in 150 ml of pet. ether (60-80°) and cooled overnight. About 10 g of light tan powder 4-nitro-3-pentadecylphenol separated. This on further two crystallization from the same solvent gave the desired product. Yield 8.0 g. m.p. 70-71°C.

Analysis Found C 72.45, H 10.33, N 4.07%

C₂₁H₃₅NO₃ required C 72.16, H 10.10, N 4.01 %

The filtrate was used for the isolation of the 6-nitroisomer which was crystallized from ethyl alcohol. Yield 3g. m.p. 39°C.

3.3.4 4-amino-3-pentadecyl phenol

i) 4-nitro-3-pentadecyl phenol 1.75g (7_m mole) was taken in 100ml round bottom flask, containing 25 ml of absolute alcohol. To this, 0.80ml (20mmoles) of 98% hydrazine hydrate and 0.2g of Rincy nickel catalyst were added. Then the whole solution was refluxed on the water bath for 3-4 h. After this period, the solution was filtered, concentrated and cooled to 0°C, when 4-amino-3-pentadecyl phenol separated.

It was recrystallized from ethanol, to give light brown coloured crystals. Yield 1.0 g, m.p. 106°C.

Analysis found C 79.09, H 11.28, N 4.02%

$C_{21}H_{37}NO$ requires C 78.94, H 11.67, N 4.38%

ii) 7.5 g (0.025 mole) of 3-pentadecyl phenol dissolved in 3.9g (0.0687 mole) of potassium hydroxide in 50 ml of 95% ethyl alcohol was placed in 1 litre, 3 neck round bottom flask fitted with a stirrer, thermometer and reflux condenser and was cooled to -5°C. To this was added diazonium chloride prepared from 5.25 g of sulphanilic acid dihydrate suspended in 25 ml of ethyl alcohol. The resulting red-dye solution was stirred for 2h. and was reduced by saturated solution of 11.25 g of sodium dithionite at 75°C. on a water bath. Solution of 4g. of acetic acid in 30ml of water was added to the solution and refluxed for 1h. when the red colour of the solution changed to pale tan colour. The reduced solution was poured in a beaker and was cooled to 0°C. when crude 4-amino-3-pentadecyl phenol separated. The product

was filtered off and was crystallized from petroleum ether (100-120°C). Yield 5.0 g, m.p. 105-106°C.

Analysis Found C 78.77, H 11.82, N 4.33%

$C_{21}H_{37}NO$ requires C 78.94, H 11.67, N 4.38%

2.3.5 Synthesis of N.N.- Bis (4-hydroxy -2- pentadecyl phenyl) pyromellitic diimide i.e.N.N. - bis (4-hydroxy 2 pentadecylphenyl) 1,2,4,5, benzene tetracarboxylic 1,2,4,5, - diimide : (II)

In a 100ml 4 neck R.B.flask equipped with mechanical stirrer, nitrogen gas inlet, thermowell, reflux condensor with guard tube were placed 3.19g (0.01 mol) APP and 12.5 ml of m-cresol. To this 1.0905 g (0.005mol) of pyromellitic dianhydride (PMDA) was added in small portions over a period of 10 minutes at room temperature (25°). The contents were stirred for 3 hours and then temperature raised to 220°C at which reaction stirred for 3 hours. Arrangements for distillation were made and water formed by condensation was removed azeotropically alongwith m-cresol over a period of 30 minutes. Finally most of the m-cresol was also removed and concentrated solution of reaction mixture was allowed to cool to 25°C and poured into rapidly stirred 200ml of hexanes. Yellow precipitate was filtered, washed with hexane and dried under reduced pressure at 80°/4h to yield 4.09g product (almost quantitative yields). Product diimidediol has range of melting 195-210°. Purification of diimidediol was performed by leaching with hot absolute ethanol (3x40 ml) and recrystallisation of residue from a mixture of THF and methanol. Yield of crystallised product was 3.3 g (82.4% yield) after vacuum drying at 160° for 2 hours.

The monomer is essentially polymerisation grade at this point and showed mp 220° and m/e = 820.

Elements Analysis calculated for C 76.09, H 8.78, N 3.41

found C 75.95, H 8.93, N 3.29

The same monomer (II) can be obtained from reaction in p-cresol and toluene at 130°C where water was removed azeotropically. However yields are somewhat lower (52.5% yield).

IR: 3363(br), 1772, 1734, 1720, 1616, 1582, 1500, 1384, 1122, 719 cm⁻¹ (Nujol mull)

¹H-NMR (in DMSO-d₆ ppm, d) 9.7 (2H, broad), 8.2 (4H, s), 6.5-7.2 (6H, m), 2.2 (4H, t), 1.1 (52H, s), 0.8 (6H, t).

¹³C NMR : (1 H decoupled) in DMSO-d₆ (ppm, d) 166.31, 158.86, 142.26, 137.45, 130.74, 121.21, 118.30, 116.42, 114.10, 31.84, 31.34, 30.16, 29.60, 29.28, 22.59 and 14.13

DEPT : quaternary carbons : 166.31, 158.86, 142.26, 137.45 and 121.26.

CH = 130.74, 118.30, 116.42 and 114.10

CH₂ = 31.84, 31.34, 30.16, 29.60, 29.28 and 22.59

CH₃ = 14.13

Preparation of Amide acid (I) in NMP and subsequent imide there from.

In a three neck 100ml round bottom flask : equipped with nitrogen gas inlet: magnetic stirrer, thermowell and calcium chloride guard tube were placed 0.638g (2 mmol) of APP and 6ml of dry NMP. Solution was stirred at 0°C and 0.218g (1 mmol)

of PMDA was added in small portions. Reaction mixture was stirred at 0°C for two hours and then allowed to attain 25°C at which it was stirred for twelve hours. Clear solution was observed, which was divided into three parts.

I) A part of the above solution (2ml) was poured into excess of ice-cold water and the precipitate was filtered, washed with ice water and dried under vacuum at room temperature.

II) Chemical Cyclisation: Second part of solution (2ml) was mixed with 2ml of dehydrating mixture (1:1, acetic anhydride:Pyridine) and stirred for several hours at 25°C. (Precipitation was observed within 10 minutes of addition.) The separated solid was filtered, washed with hexane and dried under vacuum.

III) Thermal imidisation : Third part of solution (2ml) was heated at 120°C at 1mm of Hg, to complete I) remove the solvent and heating was continued for additional 3 hours. Hexane was added to washed residue, filtered and solid dried under vacuum.

Each sample I) to III) was analysed by IR spectroscopy.

2.3.6 AROMATIC DIACID CHLORIDE

2.3.6.1 Synthesis of isophthaloyl chloride (IPC)

(Note : The whole reaction was performed in a fume cupboard)

A 250 ml three necked round bottom flask was equipped with reflux condenser and a dropping funnel isophthalic acid, 35g(0.21 mole) was added to the flask. Then 75ml (122g.1.05mole) of thionyl chloride was added dropwise through dropping funnel,

The flask was occasionally shaken during the addition of thionylchloride. Then 3ml of dry pyridine was added through dropping funnel. The reaction mixture was refluxed for 6 hours. The excess thionyl chloride was removed by distillation and finally under vacuum. The reaction product was then distilled at 95°C/1mm and the distilled product was finally recrystallised from dry n-hexane (10ml hexane for 20gm acid chloride) at 25°C.

The yield of the product was 40.5 (96.4%) and its melting point was 41-42°C.

Elemental Analysis calculated for : $C_8H_4O_2Cl_2 =$

C 47.39, H 1.97, Cl 34.97%

C 47.40, H 1.95, Cl 34.68%

2.3.6.2 Synthesis of terephthaloyl chloride (TPC)

(Note :The whole reaction was performed in a fume cupboard)

In a 250ml round bottom flask equipped with a reflux condenser and a dropping funnel were placed 35g (0.21 mole) of terephthalic acid. This was then reacted with 75ml (1.05 mole 122gm) of thionylchloride in the presence of 3 ml of dry pyridine. Further experimental procedure is same as described for IPC. The distilled product (115°/3mm) was recrystallised from n-hexane. (1g/7ml).

The yield of the product was 39.8g (93.36%) and its melting point was 81-82°C.

Elemented Analysis calculated for $C_8H_4O_2Cl_2 =$

C 47.39, H 1.97, Cl 34.97%

found C 47.31, H 1.95, Cl 34.6%

2.4 PREPARATION OF POLY(ESTER-IMIDE)FROM II AND TPC

A typical procedure is described below for polymer 'A' synthesis.

In a four neck round bottomed 100ml flask equipped with nitrogen gas inlet; condenser and calcium chloride guard tube were placed 0.820g (1m mol) of diimide bisphenol (II) and 4ml of the dry solvent-N-methylpyrrolidone containing 24mg. of anhydrous LiCl. The solution was stirred under nitrogen and 0.203g (1 mmol) of terephthaloylchloride (TPC), were added at 25°C. The mixture was stirred for 30 minutes and then 1ml of dry pyridine was added. The temperature raised to 80°C and maintained for 6 hrs. Reaction solution cooled to room temperature and poured into excess of distilled water under stirring. The precipitate was filtered, washed with water (till Cl free) and dried. The product, poly(ester-imide) was purified by dissolving in NMP and reprecipitating in methanol. Precipitate was filtered, washed with methanol and dried at 70°C for 8 hours at reduced pressure. 0.40g polymer was obtained, 84.2% yield.

Poly(ester-imides) B and C were prepared following same procedure.