

3 Experimental

3.1 Materials:

1. 1,4 Benzenediamine (BDA), (p-phenylenediamine) (LOBA CHEMIE) was commercially available. It was vacuum sublimed twice just before the polymerisation. White shining crystals were protected from light and air.
2. Bis-(4-aminophenyl)-ether, (ODA) (EGA-CHEMIE Germany) was crystallised from tetrahydrofuran and dried under vacuum.
3. N,N-dimethylacetamide (DMAC) was obtained from [M/s ROBERT JOHNSON] and was purified by distillation at reduced pressure over phosphorous pentoxide. The fraction distilled at 53°C / 11 mm was collected.
4. 2-Methyl-1,4-benzenediamine (MBDA), 2-pentadecyl-1,4-benzenediamine (PBDA), isophthaloyl chloride (IPC) and terephthaloyl chloride (TPC) were synthesised in the laboratory as described below.

3-Methyl-4-nitrosophenol :

In a 250 ml three neck round bottom flask equipped with dropping funnel, thermowell and an efficient mechanical stirrer, were placed 6.894g (0.063 mol) m-cresol, 2.79g sodium hydroxide (0.0675 mol), 6.68g (0.096 mol) sodium nitrite in total 150 ml of distilled water.

Reaction mixture was cooled to -5°C by using ice-salt bath and with stirring a mixture of 15g concentrated

sulfuric acid and 40 ml water was slowly added dropwise over a period of 1 hour. The temperature of the reaction mixture was maintained at -3°C to 0°C and stirring continued for additional 2 hour at 0°C . The yellowish precipitate was filtered, washed with ice cold water and dried in air.

For purification, product was dissolved in saturated sodium carbonate solution and filtered through cotton plug to remove any undissolved matter. Filtrate was acidified with dilute sulfuric acid at room temperature to give yellow coloured precipitate. It was filtered and washed with ice cold water till acid free and the dried compound was crystallised from 50 % alcohol.

Yield 6.53 g, m.p. 158°C

analysis Found C 62.59, H 5.40, N 10.43 %

Calculated for $\text{C}_7\text{H}_7\text{N O}_2$: C 62.75, H 5.11, N 10.22 %

2-Methyl-2,5-cyclohexadiene-1,4-dionedioxime

2.57g (0.0187 mol) of 2-methyl-4-nitrosophenol was dissolved in 26 ml of 50 % ethanol in 100 ml 3 neck round bottom flask, fitted with magnetic stirrer, reflux condenser, thermowell, and placed in an oil bath.

The reaction mixture was heated to $60-65^{\circ}\text{C}$ and to the reaction mixture 1.435g (0.020 mol) of hydroxylamine hydrochloride in 8 ml of 50 % ethanol was added through a dropping funnel. Heating and stirring was continued for 3

hours at reflux temperature, and then allowed to cool. Solution was poured into distilled water to get brown coloured precipitate, which was filtered, washed with water and dried.

yield 1.97 g, m.p. 236°C .

Analysis : Found C 55.10, H 5.37, N 18.14 %

Calculated for $\text{C}_7\text{H}_8\text{N}_2\text{O}_2$: C 55.26, H 5.26, N 18.42 %

Mass : (M^+) = 152.

3.2 2-Methyl-1,4-benzenediamine (Toluene-2,5-diamine) (MBDA)

In a 100 ml three neck round bottom flask equipped with magnetic stirrer, dropping funnel, thermowell, reflux condenser were placed 2 g of 2-Methyl-2,5-cyclohexadiene-1,4-dionedioxime alongwith 0.4 g of Raney Nickel catalyst, with the help of 20 ml of ethyl alcohol. Flask cooled in ice-bath and 3.5 ml of hydrazine hydrate was added slowly whereupon brisk effervescences were seen. Reaction mixture was stirred at $0-5^{\circ}\text{C}$ for 30 min, at 25°C for one hour and at 60°C for about 3-4 hours. The homogeneous brown coloured solution was filtered to remove catalyst. Formation of product was checked by TLC. From filtrate, alcohol was removed by distillation and residue was distilled under reduced pressure, b.p. 110°C /4mm. Crystallisation from petroleum ether offered pure diamine yield 1.6 g, m.p. 63°C .

It was stored under nitrogen

Analysis : Found C 68.81, H 8.38, N 23.20 %

Calculated for $C_7H_{10}N_2$: C 68.85, H 8.20, N 22.95 %

Mass : (M^+) = 122

3.3 Cashewnutshell liquid and Anacardol

The refined cashewnut shell liquid was used throughout the present investigation.

3-Pentadecenyl phenol (Anacardol)

Raw commercial cashewnutshell liquid (heat extracted) (900g) was distilled under vacuum. The flask was heated slowly till the initial frothing subsided and distillate was collected between 190-220°C / 2-4 mm Hg pressure. This was redistilled to give pale yellow anacardol.

Yield 410g, b.p. 195 - 200°C / 2 mm [8]

Analysis : Found C 83.80, H 10.56 %

Calculated for $C_{21}H_{32}O$: C 83.94, H 10.76 %

3-Pentadecylphenol (Tetrahydroanacardol)

Cardanol (Anacardol) (330 g) was hydrogenated at 70°C in a 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.

Recrystallisation from pet ether (40-60°C) gave white waxy solid 3-pentadecyl phenol.

Yield 270g, m.p. 50-51°C [9]

4-Amino-3-pentadecylphenol via diazonium salt

7.5g (0.025 mol) of 3-Pentadecylphenol dissolved in 3.9g (0.0687 mol) of potassium hydroxide in 50 ml of 95 % ethyl alcohol was placed in one litre, 3 neck round bottom flask equipped with an efficient stirrer, thermometer and reflux condenser and was cooled to -5°C. To this was added diazonium chloride prepared from 5.25g of sulphanilic acid dihydrate suspended in 25 ml of ethyl alcohol. The resulting red-dye solution was stirred for 2 hours 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 30 ml water was added to the solution and refluxed for 1 hour, when the red colour of the solution ~~was~~ changed to pale tan colour. The reduced solution was poured in a beaker and was cooled to 0°C, when crude 4-amino-3-pentadecylphenol separated. The product was filtered off and was crystallized from aqueous ethanol.

Yield 5.9 g, m.p. 105-106°C.

Analysis :Found C 78.77, H 11.82, N 4.33 , O 5.08 %

Calculated for $C_{21}H_{37}NO$:C 78.94, H 11.67, N 4.38 ,

O 4.99 %

IR : 3200, 3300 cm^{-1} (NH_2)

Mass : (M^+) = 319.

2-Pentadecyl-2,5-cyclohexadiene-1,4-dione. (2-Pentadecyl
1,4-benzoquinone)

5.752g (0.018 mol) of 4-~~a~~mino-3-pentadecylphenol was placed in a 500 ml 3 neck round bottom flask equipped with reflux condenser, thermometer and an efficient stirrer. A mixture of sulfuric acid (9.17 g) and distilled water (100 ml) was added to the flask and mixture stirred. A solution of potassium dichromate 3.5g dissolved in 55ml of distilled water was added with constant stirring and heated to 60°C . Reaction mixture was stirred for additional 2 hours at 60°C and allowed to cool to room temperature. Product was filtered out and washed with distilled water till acid free and dried. 2-Pentadecyl-1,4-benzoquinone was recrystallised from acetone to get pure product.

Yield 3.4 g m.p. $77-78^\circ\text{C}$ [33]

Analysis Found : C 79.02, H 10.83, O 10.15 %

Calculated for $\text{C}_{21}\text{H}_{34}\text{O}_2$: C 79.12, H 10.68, O 10.20 %

IR : 1664 cm^{-1} ($>\text{C} = \text{O}$)

Mass : (M^+) = 318

2-Pentadecyl-2,5-cyclohexadiene-1,4-dionedioxime (2-
Pentadecyl-1,4-benzoquinone dioxime)

3.18g (0.01 mol) of 2-pentadecyl-1,4-benzoquinone and 30 ml of 80 % ethyl alcohol were placed in a 250ml three neck round bottom flask fitted with an efficient stirrer, thermometer and reflux condenser. The mixture was stirred and heated to about 65°C. A solution of hydroxylamine-hydrochloride, 2.1g in 10 ml 80% ethyl alcohol, was added dropwise over a period of 5 minutes. Reaction mixture was stirred at reflux temperature (80 ± 2°C) for 12 hours, cooled and diluted with distilled water. The brown coloured precipitate was filtered off, washed with petroleum ether (60-80°C) and dried. It was recrystallised from 50 % ethyl alcohol.

Yield 2.8 g, m.p. 173°C [33]

Analysis : Found C 72.65, H 10.38, N 7.77, O 9.20 %

Calculated for C₂₁H₃₆N₂O₂ : C 72.31, H 10.33, N 8.03,

O 9.22 %

Mass : (M⁺) = 348

3.4 2-Pentadecyl-1,4-benzenediamine (PBDA)

3.48g (0.01 mol) of 2-pentadecyl-1,4-benzoquinone dioxime was placed in a 100 ml 3 neck round bottom flask equipped with stirrer, reflux condenser, thermowell and dropping funnel. 0.7g Raney Nickel catalyst was added cautiously, with the help of 40 ml ethanol.

To the reaction mixture, cooled at 0°C by ice-bath was added 6.1 ml of hydrazine hydrate dropwise over a period of 10 minutes, contents stirred for 20 minutes and ice-bath removed to allow reaction mixture to attain room temperature (25°C). Brisk effervescences of evolving gas were seen. Stirring was continued for additional 3-4 hours at room temperature. Reaction mixture was refluxed for one hour and then cooled to 25°C and contents were filtered to remove catalyst. Filtrate was subjected to distillation to remove solvent and further distillation of residue under reduced pressure gave 2-pentadecyl-1,4-benzenediamine. It was recrystallised from petroleum ether.

Yield 1.85 g, m.p. 62-63°C.[33]

Analysis : Found C 79.33, H 12.14, N 8.39 %

Calculated for $C_{21}H_{38}N_2$: C 79.24, H 11.95, N 8.80 %

Terephthaloyl chloride (TPC) and Isophthaloyl chloride (IPC)

Caution : (Experiment performed in fuming cupboard)

In a 500 ml perfectly dry round bottom flask equipped with reflux condenser, guard tube (anhydrous calcium chloride filled) were placed 50g (0.246 mol) terephthalic acid and 250g (2.10 mol) of thionyl chloride alongwith 1 ml pyridine as a catalyst. Reaction mixture was heated to

reflux and after 12 hours reaction, no more HCl gas was found to evolve. Excess thionyl chloride was removed by distillation. Residue was distilled under reduced pressure, b.p. 115°C / 3 mm. Recrystallisation from dry hexane gave product, m.p. $81-82^{\circ}\text{C}$ which was stored in inert atmosphere in dry box.

Under similar conditions, IPC was obtained b.p. 103°C / 1.5 mm, m.p. $43-44^{\circ}\text{C}$.

A typical procedure for polycondensation is described below :

3.5 Polyamide(D) from MBDA and TPC by Interfacial polycondensation :

In a high speed stirring reactor (household blender-mixer) were placed 0.122g (0.001 mol) of MBDA and 0.106g (0.001 mol) of sodium carbonate in 8 ml of water at 0°C . Added to this was 0.203g (0.001 mol) of TPC in 5 ml of chloroform at the same temperature and the mixture was stirred for 15 minutes. Finally, the contents (alongwith the precipitated polymer) were poured into 200 ml of methanol. The polymer was separated by filtration, washed with water, acetone and methylene chloride, and dried under vacuum at 80°C for 10-12 hours. The yield was 0.310 g (60%). The inherent viscosity of the polymer in

concentrated sulfuric acid was 0.68 dL/g, measured at a concentration of 0.5 g/dL, at 30°C. Other polymers were prepared by analogous procedures.

Polyamide(D) from BDA and IPC by solution polycondensation

Under the flow of nitrogen, in a flask with CaCl₂ guard tube, 0.203g (1 mMol) of IPC was added to a solution of 0.108g (1 mMol) of BDA in 5 ml of N,N-dimethylacetamide at -10°C. The solution was stirred at 0°C for 60 minutes and at 25°C for 20 hours, and poured into 200 ml of methanol. The isolated polymer was thoroughly washed with methanol and dried at 100°C in vacuum-oven. The yield was 0.904 g (95.1 %). The inherent viscosity of the polymer in concentrated sulfuric acid was 0.58 dL/g measured at a concentration of 0.5 g/dL at 30°C.

In a similar fashion other polyamides by solution polymerisation were obtained.

3.6 Instrumental Methods

Ubbelohde viscometers were used to determine inherent viscosities of polymer solution having concentrations of 0.5 g/100 ml in concentrated sulfuric acid. A constant temperature bath was maintained at 30°C.

Thermogravimetric and DSC analysis were simultaneously obtained with a Rigaku TG-DSC 8110 analyser in air environment. All samples were powders and sample sizes varied from 2 mg to 3 mg. Heating rate used for the determinations was 10^oC/min.