

## SYNTHESIS AND CHARACTERIZATION OF SOLUBLE AROMATIC POLYAMIDES FROM 2,5-BIS (3-AMINO-PHENYL 3,4-DIPHENYL)-, 4-DIPHENYLTHIOPHENE AROMATIC DIACID CHLORIDE.



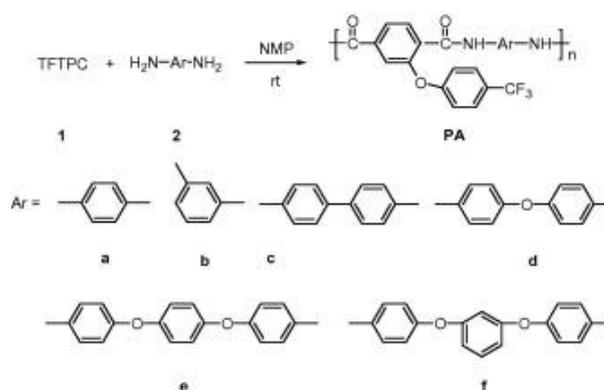
P. H. Basutkar

D.B.F. Dayanand College of Arts & Science, Solapur.

### ABSTRACT:-

A novel aromatic diamine namely 2,5-bis(3aminophenyl)-3, 4- diphenylthiophene (IX) was synthesized and characterized by technique such as, IR,NMR, and mass spectroscopy.

A new series of aromatic polyamides was synthesized by low temperature solution condensation of IX with acid chlorides such as terephthaloyl chloride, (TPC) and isophthaloyl chloride(IPC) in DMAc. The co-polyamides were also prepared from diamine (IX) and TPC and IPC in different mole proportion under similar experimental conditions. The viscosities of polyamides were in the range from 0.16-0.31 dL/g. The polymers were also characterized by IR spectroscopy, solubility tests, and thermal properties. The polyamides and Co-polyamides obtained are soluble in amide type solvents. These polyamides showed initial decomposition temperature (To) in the range of 382-420<sup>0</sup>C in nitrogen atmosphere indicating high thermal stability.



**KEY WORDS:** 2,5-bis(3-aminophenyl)-3,4-diphenylthiophene, terephthaloyl chloride, isophthaloyl chloride, phenylated poly(amide)s; thermal properties.

### INTRODUCTION:-

High temperature stable polymers are increasingly in demand as performance material for industrial and aerospace applications. The aromatic polyamides, polyimide and poly (amide-imide)s are well known for their excellent thermal stability, and they find use in various high temperature applications especially as strong fibre and tough films. However aromatic polymers are difficult to fabricate because of their limited solubility in common organic solvents. The solubility can be enhanced by incorporation of flexible linkage like ether, sulphide, sulfone, carbonyl, silane or cardo groups in polymer backbone.<sup>1-4</sup> The introduction of pendant phenyl group is one of the approach for improving the solubility and thereby the processability. Imai etal synthesized the polyamide, polyimide and poly (amide-imide)s<sup>5</sup> with introduction of pendant groups such as tetra phenyl thiophene moiety. The introduction of polar groups in the polymer also increased the solubility<sup>6</sup>. Soluble and thermally stable polyamides, polyimides and poly(amide-imide)s polymers from phenylated aromatic diamine (IV) have been reported<sup>7</sup> by us earlier. These polymers were derived from 2, 5-bis(4-aminophenyl)3, 4-diphenyl thiophene. However there are no reports on corresponding bis-(3- aminophenyl)-diamine and polymers therefrom having meta catenation. Therefore we have studied the synthesis and characterization of novel corresponding bis-(3- aminophenyl)-diamine containing bulky pendant phenyl group.

Thus in the present investigation we report the synthesis of novel phenylated aromatic m-oriented diamine containing pendant phenyl groups, 2,5,-bis(3-aminophenyl)-3,4-diphenyl thiophene (IX), it's sepctral

characterization by IR, NMR, and Mass and the preparation of a series polyamide and co-polyamides from (IX). IR spectral data, viscosity, solubility and thermal characteristics of these polymers are also discussed.

## EXPERIMENTAL MEASUREMENTS

Viscosity measurements were made with a 0.5% polymer concentration in N, N- dimethylacetamide (DMAc) at 30<sup>o</sup> C using suspended type Ubbelohde viscometer. The solubility of the polyamide and co-polyamide were determined at a 3% concentration in various solvents. Transmission IR spectra were recorded on a Perkin-Elmer 883 IR spectrophotometer as a KBr pellet or polymer film. <sup>1</sup>H-NMR spectra were recorded in DMSO-d<sub>6</sub> on a Bruker 90 MHz spectrometer using tetramethylsilane (TMS) as an internal standard reference where as <sup>13</sup>C-NMR spectra were recorded on a Bruker 200 MHz spectrometer. Mass spectra were recorded on an HMS-30 double-beam mass spectrometer. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analyses were performed on a Perkin-Elmer DSC-7 and a Perkin-Elmer TGA-7, respectively at a heating rate of 10<sup>o</sup>C/min under a flow of nitrogen gas.

### Materials

Terephthaloyl chloride (TPC), isophthaloyl chloride (IPC), were synthesized from the corresponding acids using a reported procedure and were purified by vacuum distillation followed by recrystallization from dry hexane before use. Toluene, pyridine, and DAMC were purified and dried by following the standard procedure.

### Synthesis of Monomer:-

(IX) was synthesized from IV which was prepared as in the literature [5].

### Synthesis of 2, 5-bis (4-aminoacetylphenyl)-3,4- diphenyl thiophene (V)

In a 500-mL round bottom flask were placed 24.418 g (0.0608 mol) (IV), 210 mL of glacial acetic and 14.35 g (15.2 mL 0.147 mol) acetic anhydride were added maintaining temperature at 50-60<sup>o</sup>C over a period of 1.5 h. The mixture was stirred at 100<sup>o</sup> for 1.5 h and cooled to 25<sup>o</sup> C. The solid was filtered and diacetyl derivative (V) was recrystallised from glacial acetic acid. Yield 25 g (83.35%), M.P. 317<sup>o</sup>C (by DTA), I.R. 3250 (NH) and 1660 cm<sup>-1</sup> [CONH].

### Preparation of 2,5-bis (3-nitro,4-amino acetyl phenyl)-3, 4diphenyl thiophene (VI)

In a 500 mL round bottom flask 14.73 g (0.249 mol) (V), 112 mL glacial acetic acid, 15.63 mL distilled water and 1.1 mL acetic anhydride were added. To this mixture 5.58 mL concentrated nitric acid (70% HNO<sub>3</sub>, d1.40 g/cm<sup>3</sup>) was added at once and stirred for 10 min. at 45<sup>o</sup>C and 10 min at 75<sup>o</sup>C. Then the reaction mixture was immediately cooled to room temperature and kept overnight. Bright yellow solid (VI) separates. It was filtered, washed with cold glacial acetic acid and recrystallised from acetic acid. Yield 7.4 g (50%), M.P. 214<sup>o</sup>C, IR 3340 (-NH), 1700 (-CONH), 1540 and 1350 cm<sup>-1</sup> (-NO<sub>2</sub>), NMR: <sup>1</sup>H(S) 10.25 (S, 2H), 6.7-8.7 (m, 16H), 2.2 (S, 6H).

### Preparation of 2,5-bis (3-nitro,4-amino phenyl)-3, 4-diphenyl thiophene (VII)

7.14 g (0.0125 mol) VI, 50 mL methyl alcohol and 1.25 g solid potassium hydroxide were stirred for 1 h in 250 mL R.B. flask. After one hour additional 1 g solid potassium hydroxide was added and stirring was continued for 16 h. The volatile solvent was removed by vacuum and the solid (VII) was treated water, filtered, washed with distilled water and dried. Yield 6.2 g (97.6%), M.P. 220-222<sup>o</sup>C, IR 3520, 3480, 3300, 3260 (-NH), 1420 and 1350 cm<sup>-1</sup> (-NO<sub>2</sub>), Mass:-m/e 508 (M<sup>+</sup>) NMR: <sup>1</sup>H(d) 8.0 (d, 2H), 7.2-6.7 (m, 12H), 6.5 (d, 2H), 5.96 (S, 4H, NH<sub>2</sub>).

### Preparation of 2,5-bis (3-nitrophenyl)-3, 4-diphenyl thiophene (VIII)

In a 500 mL three neck round bottom flask equipped with reflux condenser, 13.6 g (0.0268 mol) (VII) dissolved in a mixture of 309 mL of ethyl alcohol and 70 mL benzene was heated on a water bath at 80-90<sup>o</sup>C. To the hot reaction mixture 5.77 mL concentrated sulphuric acid were added and gently swirled the liquid, till the clear solution was obtained. The water bath was removed and 5.77 g (0.0844 mol) powdered sodium nitrite

were added in two lots. The mixture was stirred well and the flask was again heated on water bath as long as gas evolved (1/2 h). The reaction mixture was allowed to cool at room temperature for 10 min. and further cooled to 10°C in an ice bath. The solid was filtered and washed with water. The crude solid was extracted with hexane. The hexane solution on concentration gave (VIII) as yellow solid. Yield 6.85g (61%), M.P. 162°C, IR 1524,1346 cm<sup>-1</sup> NO<sub>2</sub>. The elemental analysis for C<sub>28</sub> H<sub>18</sub> O<sub>4</sub> N<sub>2</sub> S calc. C, 70.29%, H,3.77%, N,5.86% S,6.70%, found C, 70.18%, H,3.79%, N, 5.85%, S,6.85%, Mass (m/e) 478(M<sup>+</sup>).

#### Preparation of 2,5-bis (3-aminophenyl)-3, 4diphenyl thioiphenene (IX)

To a mixture of 10g (0.0239 mol) VIII and 100mL acetic acid, a solution of 52.9 g(0.234 mol) stannous chloride dihydrate dissolved in concentrated hydrochloric acid (21 mL) was added at once. The solution was heated on oil bath with stirring at 100°C for 4 h. Then the reaction mixture was cooled and neutralised by 353 mL of 40% aqueous sodium hydroxide solution so that diamine precipitates. This mixture was stirred for 30 minutes and was poured into ice water. The crude diamine (IX) was filtered, washed with water and dried. The diamine was purified by column chromatography. Yield 3.06 g(53%), M.P. 205-207°C., IR : 3433, 3333cm<sup>-1</sup> (NH<sub>2</sub>).

The elemental analysis for C<sub>28</sub> H<sub>22</sub> N<sub>2</sub>S calc. C, 80.38%, H,5.28%, N,6.70% S,7.65%, found C, 80.21%, H,5.22%, N, 6.58%, S,7.52%, Mass (m/e) 418(M<sup>+</sup>).

Terephthaloyl chloride (TPC), isophthaloyl chloride (IPC) were synthesised from the corresponding acids and purified by vacuum distillation, recrystallised from dry hexane before use. Toluene, pyridine and DMAc were purified and dried by following the standard procedure.

#### Synthesis of polymer: (PA-1) from IX and IPC.

In a 100ml three neck round bottom flask equipped with a magnetic stirrer, nitrogen gas inlet, calcium chloride guard tube (IX) 0.418 g(0.001 mol) and dry DMAc (3ml) were added. The mixture was stirred under nitrogen atmosphere. The reaction flask was cooled to -15°C with the help of ice-salt mixture. Isophthaloyl chloride 0.203 g(0.001mol) solid was added in two lots and stirring was continued for 2h at 0°C. Then the mixture was stirred for 12h at 25°C, and neutralised with lithium carbonate 0.075g (0.00104 mol) and heated at 80°C for 20 min. It was then degassed under vacuum and the polymer was precipitated by adding reaction mixture to excess of rapidly stirred methanol. The polymer was washed with water and finally with methanol. It was dried at 80°C under vacuum for 6h. Yield was 0.44g(80%), and reduced viscosity was 0.2dL/g.

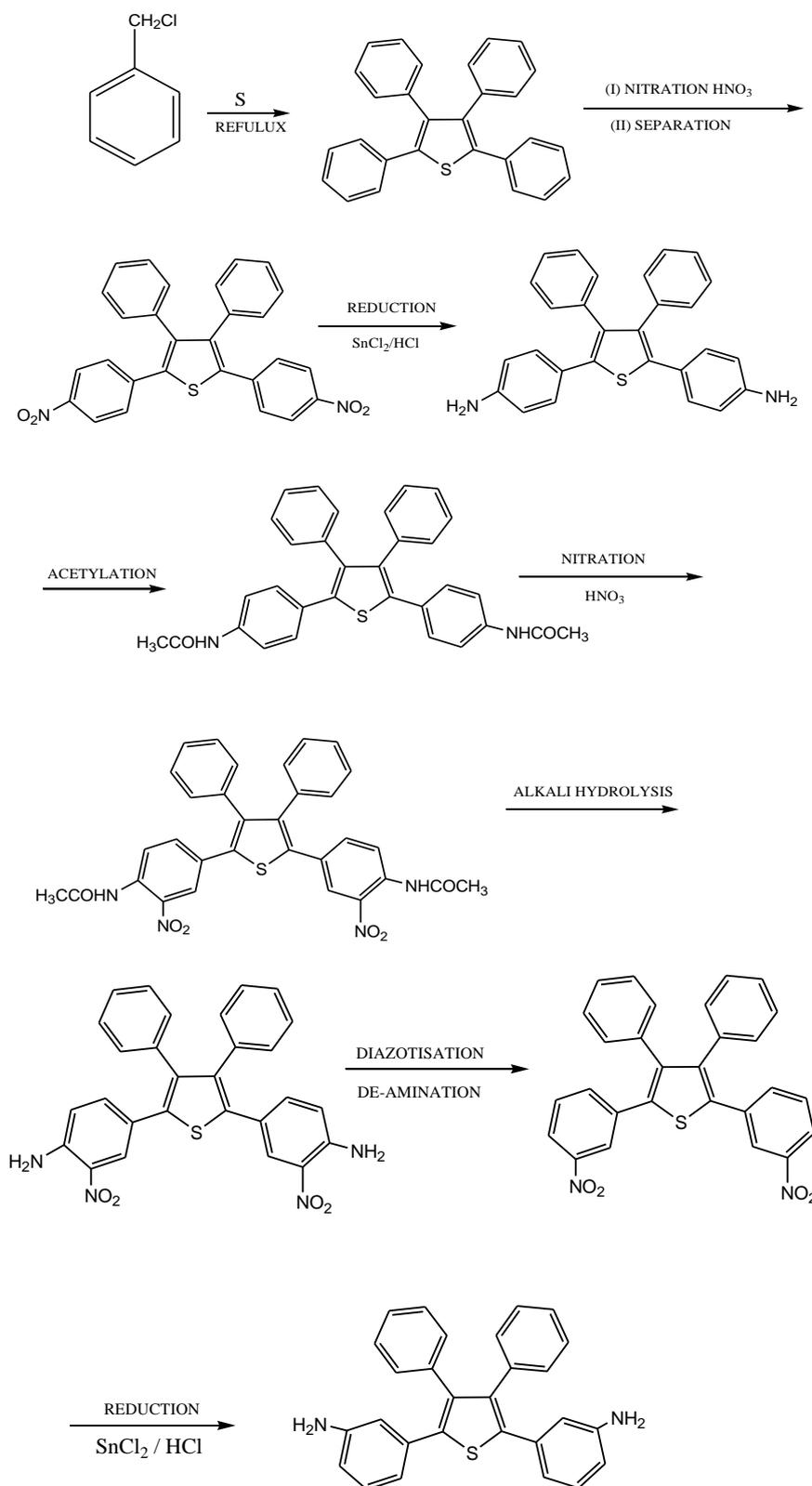
Following similar procedure polyamide and co-polyamides (PA-2 to PA -5) were prepared in good yields.

## RESULTS AND DISCUSSION

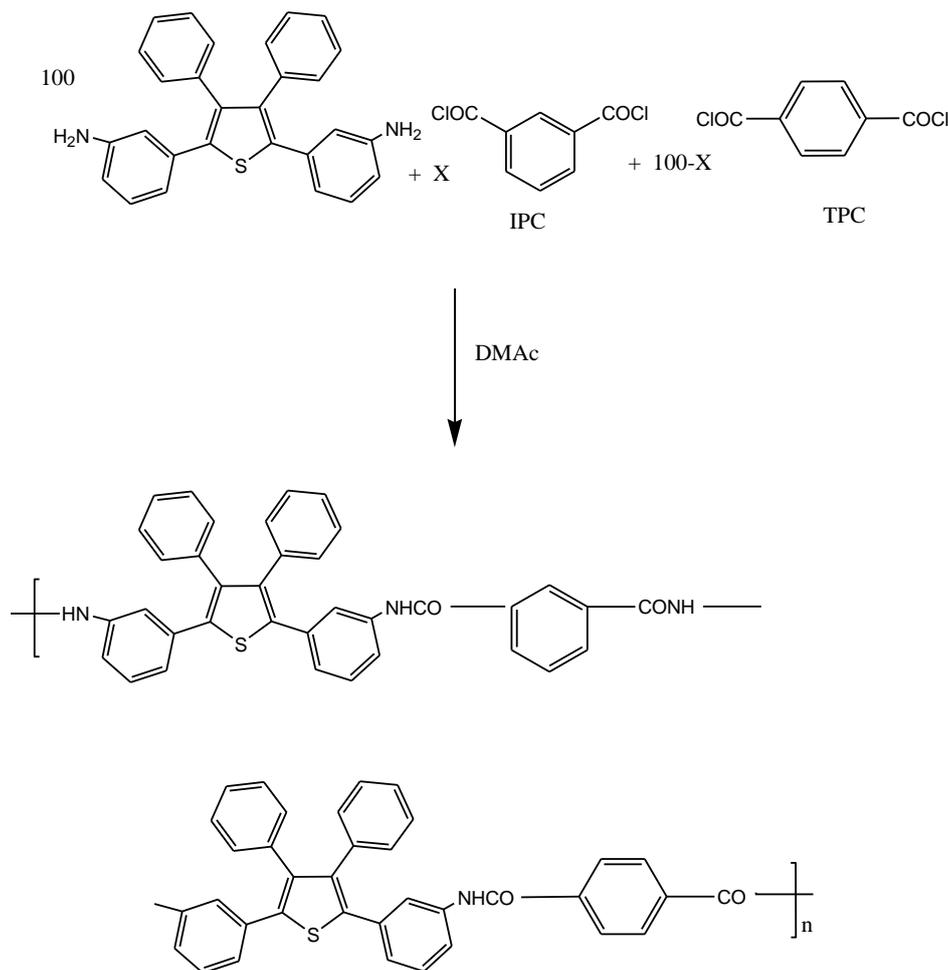
The novel diamine (IX) was synthesised from benzyl chloride in several steps. The targeted diamine with m-catenation could not be synthesised by direct nitration of TPIP and subsequent reduction of dinitro to diamines, because direct nitration yields bis-(4-nitrophenyl) structure. Therefore desired (IX) was prepared by introducing NO<sub>2</sub> group at ortho position to already existing amino groups of (IV) and then deamination to yield bis(3-nitrophenyl) moiety. The method is unambiguous on position of substitution at 3-position, since o/p-nitro substitution of (IV) is expected and p-position is blocked [hence not available] for entry of nitro group. Obviously incoming NO<sub>2</sub> group shall add at ortho to already existing NH<sub>2</sub> groups of (IV). Before actual nitration of (IV) NH<sub>2</sub> are acetylated yielding (V) which avoids oxidation of -NH<sub>2</sub>. Therefore diacetyl derivative (V) was nitrated to yield 3,3' dinitro product (VI). Thus proper sequence of reaction was planned to synthesize m-catenated diamine (IX) (SCHEME-I). To begin with (IV) was obtained as per procedure in literature(6). The (V) was obtained by acetylating (IV) with acetic anhydride. The (V) was characterized by IR spectroscopy. The infrared spectrum of (V) showed the characteristic absorption bands at 3360 (-NH-) and 1660 cm<sup>-1</sup> (CONH-). Absorptions at 3460 and 3440 cm<sup>-1</sup> were absent, indication total acetylation of (IV). The (V) was treated with concentrated nitric acid to yield (VI). The o-nitro anilide structure of (VI) was confirmed by IR, NMR and mass spectra. The infrared spectrum of (VI) showed characteristic absorption at 3340, (NH), 1700 (CONH) and 1540, 1350cm<sup>-1</sup> (NO<sub>2</sub>). The (<sup>1</sup>H) NMR spectrum of (VI) showed a singlet at 8.10.25 which exchange with D<sub>2</sub>O indicating NH whereas the singlet at 8.2.2 is assignable to methyl protons of amino acetyl moiety. Aromatic protons appeared at 8.7 to 6.7 as multiplet and two doublets. The mass spectrum showed the molecular ion peak at m/e 592 M<sup>+</sup> corresponding to molecular formula weight of (VI). This confirms

formation of dinitro-derivative as desired. Peaks at  $m/e$  550 and 508 correspond to molecular fragments (M-42) and (M-84) due to loss of one and two  $\text{COCH}_3$  units respectively.

**Scheme 1: Synthesis of 2,5-bis (3-aminophenyl)-3, 4diphenyl thoiphene (IX)**



## Scheme II: Synthesis of polyamides and copolyamides



The (VI) was deacetylated with alkali to yield (VII). The structure of (VII) was characterised by IR spectroscopy. The infra-red spectrum of (VII) showed characteristic absorption at 3520, 3480, 3300, 3260 (NH<sub>2</sub>) 1420 and 1350 cm<sup>-1</sup> (NO<sub>2</sub>). The absorptions at 1700, 1660 cm<sup>-1</sup> were absent indicating complete hydrolysis of (VI). The mass spectrum of (VII) showed molecular ion peak at m/e 508 corresponding to the molecular formula of (VII). <sup>1</sup>H NMR spectrum of (VII) showed singlet at 8.6.0 & exchangeable with D<sub>2</sub>O confirm amino group. Aromatic protons appeared at 8.8.0 doublet and 8.6.45 to 7.1 multiplet for phenylene and phenyl protons overlap. The absence of NMR signal at 8.10.25 and 2.22 indicated complete hydrolysis of the amino acetyl functional groups.

**Table 1 : Synthesis of polyamides and co-polyamides from 3,3 TPTPDA (ix)**

Polymer code	Diacidchloride mole %		Yields (%)	Viscosity <sup>(b)</sup> red(dL/g)
	IPC	TPC		
PA -1	100	00	80	0.20
PA- 2	75	25	68	0.16
PA-3	50	50	98	0.26
PA-4	25	75	70	0.17
PA-5	00	100	99	0.31

- a) Polymerization was carried out with 1 m mol of diamine and 1 mol of IPC/ or TPC  
 b) Measured of Concentration of 0.5 g/dL in DMAc at 30°C

**Table 2 : Thermal analysis<sup>(g)</sup> of polyamides and co-polyamides from 3,3 TPTDA (ix)**

Polymer code	Diacidchloride mole %		Ti <sup>(b)</sup> (°C)	T10 <sup>(c)</sup> (°C)	Tg <sup>(d)</sup> (°C)
	IPC	TPC			
PA -1	100	00	382	520	225
PA- 2	75	25	410	520	240
PA-3	50	50	420	520	260
PA-4	25	75	415	530	250
PA-5	00	100	420	540	260

- a) By thermogravimetry at heating rate of 10°C/min under nitrogen.  
 b) Temperature at which initial loss of mass observed.  
 c) Temperature at which 10% loss observed.  
 d) Determined by DSC.

The (VII) was diazotised and deaminated to give (VIII) which was characterized by IR spectroscopy. The infrared spectrum of (VIII) showed characteristics absorption at 1524, 1346 cm<sup>-1</sup> (NO<sub>2</sub>). The absence of absorptions at 3520, 3480, 3300, 3260 cm<sup>-1</sup> showed that complete deamination has taken place, thereby 4,4 – amino groups have been completely eliminated. <sup>1</sup>H NMR. Spectrum of (VIII) showed aromatic protons multiplet in the range of 8.745 to 6.5 where in downfield signal at 8.745 can be assigned to proton ortho to nitro-group which has no adjacent proton confirmed by singlet. Other protons appear as multiplets with desired integration and multiplicity. <sup>13</sup>C NMR spectrum of (VIII) (Fig.1) showed twelve different carbons. The NMR signals corresponding twelve type of carbons of which CH carbon appeared at 134.98, 130.66, 129.53, 128.54, 127.710, 123.93 and 122.38, whereas tertiary carbon gave NMR signals at 148.43, 141.72, 136.88, 135.71, 135.30, The carbon atom directly attached to nitro group is obviously most downfield and appeared at 148.43 as evidenced by D.E.P.T. and fully <sup>1</sup>H decoupled <sup>13</sup>C spectra (Fig. 2). The mass spectrum of (VIII) showed molecular ion peak at m/e 478 corresponding to molecular weight of (VIII). The (VIII) was further reduced to yield desired 3,3- diamine (IX) which was characterized by IR spectroscopy. The infrared spectrum of (IX) showed characteristics absorptions at 3433, 3333 cm<sup>-1</sup> NH<sub>2</sub>. The IR absorptions at 1524 and 1346 due to NO<sub>2</sub> groups were absent indicating total reduction. <sup>1</sup>H NMR spectrum of (IX) showed aromatic proton signals in the range of 8.815 to 6.95 as expected with desired integration and splitting from 18 protons. The amino group signal appears as a broad singlet at 8.16. The mass spectrum of (IX) showed molecular ion peak at m/e 418 corresponding to the molecular weight of (IX). This (IX) is m-catenated diamines isomeric with the p-catenated diamines (IV) (Slightly higher viscosities were observed wherein the yields were quantitative (>98%). The formation of relatively medium-low molecular weight polymers was observed with this meta catenated (IX), probably due to steric hindrance of bulky moieties, with respect to m-NH<sub>2</sub> groups and decreased reactivity of diamino groups at m-position. The p-catenated diamine (IV) gave high molecular weight polyamides (inherent viscosities 0.99 to 1.70 dL/g.). The low yields for PA 1,2 & 4 may be due to formation very low molecular weight fractions which could not be precipitated with methanol. These soluble fractions reduced the yields of the precipitated polymers.).

#### **Polymerization: - Polyamide from IX and IPC/TPC**

Aromatic polyamides were synthesized by condensation of (IX) with IPC or TPC by low temperature solution polymerization in DMAc. In similar manner co-polyamides were also prepared from (IX) and mixture of IPC and TPC in different mole proportions. (SCHEME-II) The viscosities and yields of these polyamides and co-polyamides are given in Table 1. The reduced viscosities of these polymers were in the range of 0.16 to 0.31 dL/g. There was no significant change in viscosities of polymers PA-2 to PA-5 as the mole percentage of TPC increased along the series.

The formation of polyamide was indicated by IR spectra. The IR spectrum of polyamide PA-1 exhibited a characteristic absorption bands at 1631 and 15.7  $\text{cm}^{-1}$  due to amide I and amide II. The absorption band at 3320  $\text{cm}^{-1}$  was of (NH). The solubility of polymers was determined in different organic solvents and it was observed that the polymers are easily soluble in aprotic polar solvents such as NMP, DMA<sub>c</sub>, DMSO, DMF pyridine and in m-cresol, but insoluble in CH<sub>2</sub>Cl<sub>2</sub>, benzene and methanol etc. The thermal properties of these polymers were evaluated by thermogravimetry and differential scanning calorimetry. The Table 2 incorporates the thermal data such as initial decomposition temperature (Ti), 10% decomposition temperature (T<sub>10</sub>) and Tg. No weight loss was observed below 380°C and Ti values increased along the series as contents of TPC increased. Decomposition of polymer structure at 10% wt loss occurred in the range of 520-540°C. following the same pattern of increase in T<sub>max</sub> with increased mol % of TPC in polyamide. The glass transition temperature for the polyamide, PA-1 is 225°C and the Tg increased upto 260°C with the increased content of rigid -p-catenated TPC moiety in the polymer

**REFERENCES;**

1. Harris, F, W, Karnavas, A, J, Das, S, Cucuras, Hergenrother, P, M, Polymer Mat Sci Eng, 1986, 54, 89.
2. Feld, W, A, Ramlingam, Harris F, W, Polym. Sci. Polym Chem, 1983, 21, 319.
3. Feld, W, A, Ramlingam, Harris F, W, Polym. Prepr, 1981, 22, 215.
4. Harris F, W, Beltz, M, W, Das, Gupta, R, K, Polym Prepr 1984, 25, 160
5. Imai, Y, Maldar, N, N, Kakimoto, M, J Polym Chem 1985, 23, 1797, 1984, 22, 2189, 1985, 23, 2073.
6. Joshi, M, D, Basutkar P, H, Lonikar, S, V, Maldar, N, N, Idage, B, B, J Appl Polym Sci. 1998, 68, 1523.