

## Synthesis And Characterization of Aromatic Polyamides Containing Ether Ketone Ether Linkages And Pendant Pentadecyl Groups

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**Abstract:** New aromatic diamines; containing ether ketone ether linkages and pendent pentadecyl groups namely; 4, 4'-bis-(4-amino phenoxy) benzophenone (4APB) and 4, 4'-bis (4''amino phenoxy-3-pentadecyl) benzophenone (4APPB) were synthesized and characterized. 4APB was synthesized in 90% yield either by condensation of 4, 4-dihydroxybenzophenone with 4-chloronitrobenzene and subsequent reduction of intermediate dinitro-ether-ketone; 4, 4'-bis (4''nitro phenoxy) benzophenone (4NPB); with hydrazine hydrate or by reaction of 4-aminophenol with activated dihalides; 4, 4'-difluorobenzophenone (DFB); in a polar aprotic solvent in presence of potassium carbonate. Similarly 4APPB was synthesized in 90% yield either by nucleophilic substitution condensation DFB and 2 moles 4-amino-3-pentadecyl phenol in the N-Methyl-2-Pyrrolidone/toluene. 4APB, 4NPB and 4APPB were characterized by FT-IR, <sup>1</sup>H, and <sup>13</sup>C NMR, and elemental analysis. Low temperature solution polycondensation of 4, 4'-bis-(4-amino phenoxy) benzophenone (4APB) and 4, 4'-bis (4''amino phenoxy-3-pentadecyl) benzophenone (4APPB) in combination with different mol % of aromatic diacid chlorides, Isophthaloyl chloride and Terephthaloyl chloride, in N-Methyl-2-Pyrrolidone gave series of the polyamides and co-polyamides containing ether-ether-ketone linkages in the main chain and pendant pentadecyl groups respectively. These aromatic polyamides / co-polyamides were obtained in greater than 90 % yield and were characterized by FT-IR, inherent viscosity, solubility tests, TGA, DSC and XRD. The polymers had inherent viscosities in the range of 0.20 – 0.75 dL/g, soluble in polar aprotic like N-Methyl-2-Pyrrolidone due to amorphous to partially crystalline morphology: as XRD pattern indicated. Polymers were thermally stable upto 340 °C due to higher content of aromatic moieties, amide links and aryl-ether, ketone, when investigated by TGA and showed glass transition temperature in the range of 230 to 341 °C depending on the constituent reactants. These new polymers are expected to find applications as gas separation membranes and engineering materials in aerospace and nuclear industries as high performance films, coatings etc.

**Keywords:** 4, 4'-bis (4''amino phenoxy) benzophenone, 4, 4'-bis (4''nitro phenoxy) benzophenone, 4, 4'-bis (4''amino Phenoxy-3-pentadecyl) benzophenone, soluble, polyamides, copolyamides, solubility, thermal properties, XRD.

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### I. Introduction

Wholly aromatic polyamides (aramids) are highly thermally stable polymers with a favorable balance of physical and chemical properties [1-3]. However, these polymers are generally intractable and lack the properties essential for successful fabrication into useful forms because of their high melting or glass transition temperatures ( $T_g$ ) and their limited solubility in organic solvents [4-7]. Therefore, a great deal of effort has been made to improve the processing characteristics of the polymers. Instead of search for new class of thermally stable polymers, efforts are concentrated on improved flexibility with minimum loss of thermal stability [8-15]. Where in emphasis was placed on the synthesis of thermally stable polymers, which include introduction of flexible groups such as ether, sulphone, aliphatic linkages, cardo groups, bulky pendant groups etc, into polymer chain replacing symmetrical aromatic rings with disturbance of rigid crystalline structure of polymer to improve their solubility [16-19]. Generally, it is more convenient to synthesize the modified aramids with the structural modification of diamine monomers, followed by the polycondensation reaction with available aromatic dicarboxylic acids or their derivatives. The most popular diamine monomer with a flexible linkage is 4, 4'-oxydianiline (ODA). Although the resulting aromatic polyamide, which is produced by the polyamidation reaction with terephthaloyl chloride, has flexible ether linkages along the main chain, it is still insoluble in organic solvents such as NMP or DMSO without lithium chloride [22–26]. The present investigation reports synthesis of new diamines viz. 4APB, 4APPB and from new series of polyamides/copolyamides to study of various properties like viscosity solubility, thermal and morphological.

## II. Experimental

### 2.1 Materials:-

4, 4'-Difluorobenzophenone (Spectrochem), (DFB) 4, 4'-Bishydroxybenzophenone (BHB) and 4-Chloronitrobenzene were used as received. IPC and TPC were prepared by reaction of thionyl chloride on the corresponding diacids and were used after recrystallization from the dry hexane. Potassium carbonate was dried at 180°C for 6-8 hr before use. 4-Aminophenol was recrystallized from ethanol. N-Methyl-2-Pyrrolidone (NMP) and Triethyl amines were dried and distilled by standard procedure and store under molecular sieve 4A<sup>0</sup>.

### 2.2 Measurements:-

Melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. FTIR spectra of organic compounds and polymers were recorded as a KBr pellet on a Perkin-Elmer 883 IR spectrophotometer. <sup>1</sup>H-NMR (200 MHz) and <sup>13</sup>C-NMR (50 MHz) spectra were recorded on a Bruker NMR spectrophotometer in DMSO-d<sub>6</sub>. Elemental Analysis was performed with a Perkin Elmer Model 2400 C, H, N and analyzer. Inherent viscosity measurements were made at polymer concentration of 0.5 g/dL in NMP at 30 ± 0.1°C using suspended level Ubbelohde viscometer. The solubility of polymers was determined at 3 wt % concentration in various solvents at room temperature or on warming if needed. Thermo gravimetric analysis was performed on Perkin- Elmer TGA-7 at a heating rate of 10°C/min. under nitrogen. DSC analysis of the polymers was performed on Rigaku Thermo flux TG 8110 at a heating rate of 10°C/min. under nitrogen. X-ray diffraction patterns of polymers were obtained on a Rigaku Dmax 2500 X-Ray diffractometer at a tilting rate of 2°/minute. Dried polymer powder was used for X-ray measurements.

### 2.3 Synthesis of monomer:-

**2.3.1. Synthesis of 4, 4'-Bis (4''amino phenoxy) benzophenone 4APB:-** It was prepared by two methods.

**Method 1:-** It involved two steps as detailed below:

#### i) Synthesis of 4, 4'-Bis (4''nitro phenoxy) benzophenone 4NPB (I):-

Distilled DMF 1.15 mL, 4, 4'-Dihydroxybenzophenone 0.214 g (1mmol), 4-chloronitrobenzene 0.315 g (2 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub> 0.276 (2 mmol) were placed in three necked round bottom flask equipped with a reflux condenser, a N<sub>2</sub> gas inlet, a magnetic stirrer, a thermowell and an oil bath. The reaction mixture was heated with stirring and was kept at 160 °C for 18 h. The mixture was allowed to cool to room temperature and poured into excess of water to precipitate yellow solid. 4NPB was collected by filtration, washed with hot water, dried and purified by crystallization from (DMF+CH<sub>3</sub>OH).

Yield- 0.435g (95%).

M. P.136-140°C.

The elemental analysis calculated for C<sub>25</sub>H<sub>16</sub>N<sub>2</sub>O<sub>7</sub>: C-65.79; H-03.51; N- 06.14 %

Found: C-65.75; H-03.50; N- 06.12%

#### ii) Synthesis of 4, 4'-Bis (4''amino phenoxy) benzophenone 4APB (II):-

In a three necked round bottom flask equipped with a magnetic stirrer, a reflux condenser, a N<sub>2</sub> gas inlet. and an oil bath; purified 4NPB 1.614g (3.54 mmol), 10 % Pd/C (0.02g) and ethanol 15 mL were stirred and hydrazine hydrate 10 mL was added dropwise at room temperature over a period of 20 min. and heated at 80°C for 6 h. The reaction mixture was filtered while hot to remove Pd/C and the filtrate was concentrated by distillation of the solvent. The residue was crystallized from toluene/ethanol (9:1) to give cream crystals.

Yield-1.14 g (92%).

MP-124-126°C.

The elemental analysis calculated for C<sub>25</sub>H<sub>20</sub>N<sub>2</sub>O<sub>3</sub>: C 75.76; H 05.05; N 07.07 %

Found: C 75.75; H 05.03; N 07.05 %

**Method -2:-** It was one step process as given below;

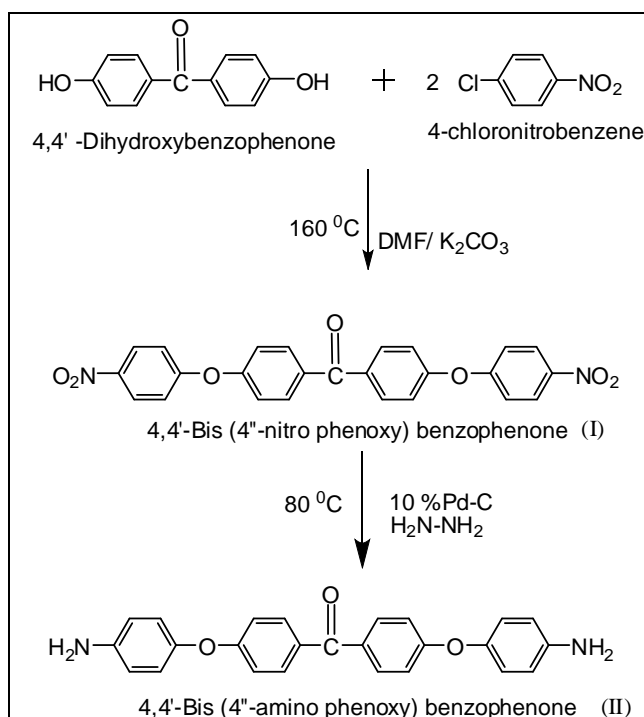
4,4'-difluorobenzophenone 0.218 g (1mmol) , 4-aminophenol 0.218g (2 mmol) and anhydrous K<sub>2</sub>CO<sub>3</sub>, 0.276g (2 mmol), 5 mL NMP, 25 mL toluene were placed into three neck round bottom flask equipped with magnetic stirrer, a Dean Stark fitted with condenser and a N<sub>2</sub> gas inlet. The reaction mixture was stirred at room temperature for 5 h, and then it was heated with stirring at 130°C. Toluene was used to azeotropically remove water produced in condensation. Then, toluene was distilled out; the reaction temperature was raised to 140 °C and kept at 140 °C for 6 h. Reaction mixture was allowed to cool to room temperature and poured to excess ice water to precipitate solid. 4APB was collected by filtration, dried at 80°C under vacuum and crystallized from toluene/ethanol (9:1) to get cream crystals.

Yield-0.180 g (92.78%).

MP-124-126°C.

### 2.3.2 Synthesis of 4-amino-3-pentadecyl phenol (4ATHA): -

Synthesis of 4-amino-3-pentadecyl phenol (4ATHA) was performed from 3-pentadecyl phenol which was obtained from cardanol (distilled CNSL) as reported by us earlier [20-21].



**Scheme.1** Synthesis of 4APB (II) by Method-1

### 2.3.3. Synthesis of 4, 4'-Bis(4''amino phenoxy-3-pentadecyl) benzophenone; 4APPB (III):-

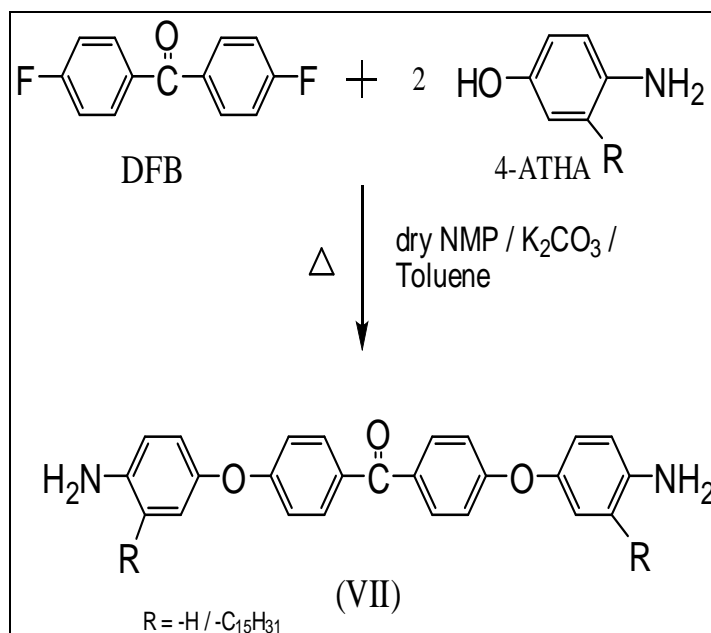
Similarly 4APPB (III) was prepared by reacting 4, 4'-Difluorobenzophenone 0.218 g (1mmol) with 4 amino 3-pentadecyl phenol using method-2.

Yield- 0.780 g. (95.58%).

MP. 62-65<sup>o</sup>C.

The elemental analysis calculated for C<sub>55</sub>H<sub>80</sub>N<sub>2</sub>O<sub>3</sub>: C 80.88; H 09.80; N 03.43%

Found: C 80.85; H 09.78; N 03.40%



**Scheme.2** Synthesis of 4APB (II) and 4APPB (III) by Method 2

### 2.3.4. Synthesis of polymers (PAPT-1to PAPT-5):-

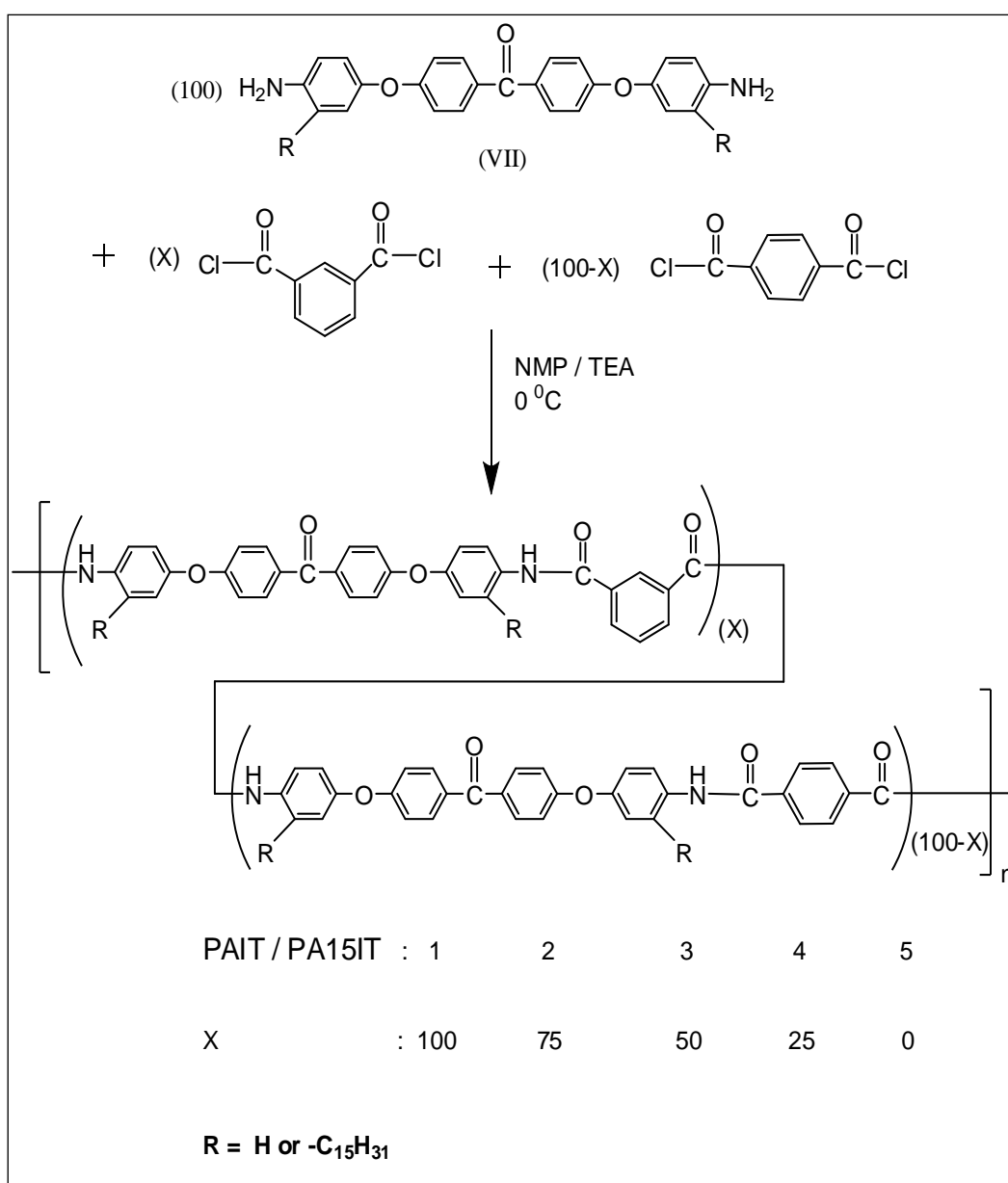
A three neck round bottom flask equipped with, guard tube, magnetic stirrer was flame dried under N<sub>2</sub> gas and then allowed to cool to room temperature. 4APB (II) 0.396 g (1m mol) was added to dry NMP 4 mL. The reaction mixture was stirred at room temperature for 10 minutes and then it was cooled to 0<sup>0</sup>C in ice-salt mixture for 20 min and acid chloride 0.203g (1 m mol), was added in small portion and this mixture was stirred at 0<sup>0</sup>C for 1 hr. Then triethyl amine 0.7 mL was added and further reaction mixture was stirred at 0<sup>0</sup>C for 2 h, then it was allowed to warm up to room temperature where it was stirred for 12 h. The viscous solution was poured into excess methanol (250 mL). The fibrous product -polymer was collected by filtration and dried under vacuum at 120<sup>0</sup>C.

Yield- 0.540 g (96%).

The same procedure was used for the preparation of PAPT-2 to PAPT-5.

### 2.3.5. Synthesis of polymers (PA15IT-1 to PA15IT-5):-

Similar procedure was used for preparation of (PA15IT-1 to PA15IT- 5) using 4APPB (III) (1mmol), with various mol % of acid chloride.



**Scheme.3** Synthesis of polyamides PAIT-1 to PAIT-5 and PA15IT-1 to PA-15IT-5 by low temperature solution method.

### III. Results and discussion

#### 3.1. Monomer synthesis and characterization:-

Two step route outlined in (Scheme.1), shows the method-1 for the synthesis of novel diamine monomer 4APB. The first step is an aromatic nucleophilic substitution reaction of 4-chloronitro benzene with potassium phenolate of 4, 4'-bihydroxybenzophenone (BHB), producing 4NPB. In the second step 4NPB was readily converted into 4APB, by reduction with hydrazine hydrate and in the presence of Pd/C (10%) catalyst in refluxing ethanol. 4NPB and 4APB were characterized by FT-IR, NMR [ $^1\text{H}$  and  $^{13}\text{C}$ ]. The 4APB was also synthesized by one step condensation of DFB and 4-aminophenol in the DMF (Scheme.2), whereas 4APPB was synthesized by one step condensation of DFB and 4-ATHA in the of NMP/toluene system. (Scheme.2). Elemental analysis of 4APB and 4APPB for C, H, and N was in good agreement with theoretical values.

##### 3.1.1. FT-IR spectrum of 4NPB:

FT-IR spectrum of 4NPB is shown in (Fig.1), which indicate two strong absorptions at 1521, 1338 ( $\text{NO}_2$  asymmetric and symmetric stretching, respectively), absorptions at 1667 and 1200  $\text{cm}^{-1}$  corresponding to CO (ketone) and -C-O-C- (ether) linkage.

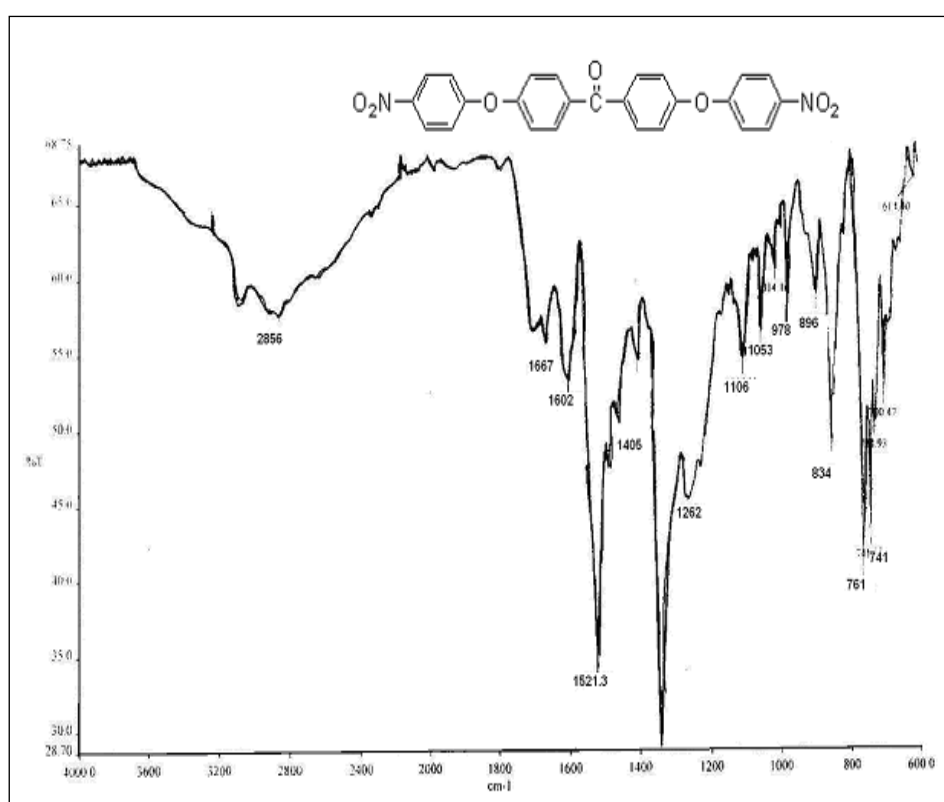


Fig.1 FT-IR spectrum (KBr) of 4NPB (I)

##### 3.1.2. $^1\text{H}$ NMR spectrum of 4NPB:

$^1\text{H}$  NMR spectrum (Fig.2), of 4NPB shows doublet of doublet at 8.36, 8.31 ppm (aromatic protons of phenyl ring with nitro group) and 7.94, 8.01 ppm (aromatic protons of phenyl ring attached to ketone group).

##### 3.1.3. $^{13}\text{C}$ NMR spectrum of 4NPB:

$^{13}\text{C}$  NMR spectrum (Fig.3) of 4NPB showed nine signals corresponding to nine different types of carbons, of which carbonyl carbon appeared at 193.8 ppm where as quaternary carbons appeared at 161.71, 159.91, 158.83 and 143.55 ppm and -CH carbons appeared at 132.53, 126.11, 119.45 and 118.49 ppm.

##### 3.1.4. DEPT $^{13}\text{C}$ NMR spectrum of 4NPB:

DEPT spectrum (Fig.4), also confirmed structure of 4NPB, all the quaternary carbons showed no signal peaks and -CH carbons appeared upside in the spectrum.

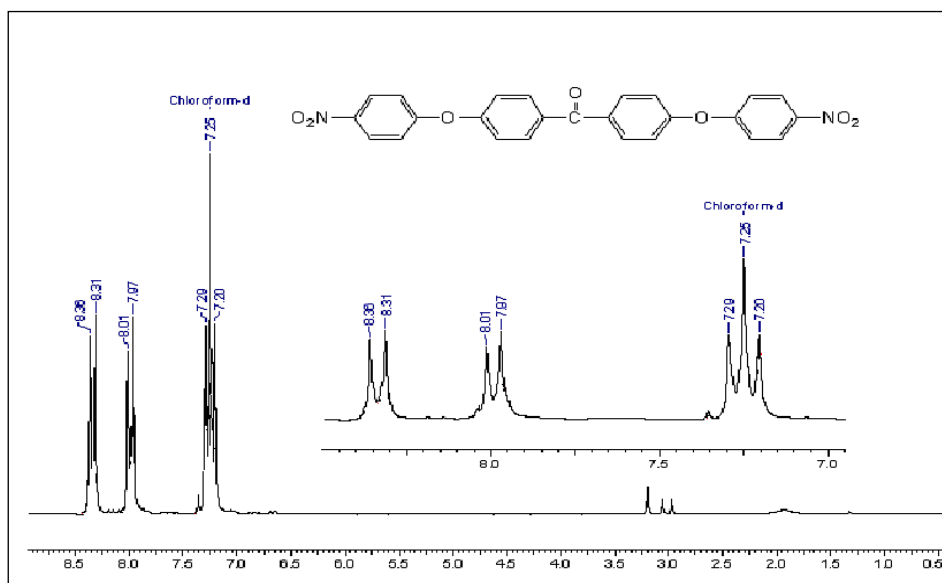


Fig.2 <sup>1</sup>H NMR spectrum of 4NPB (I)

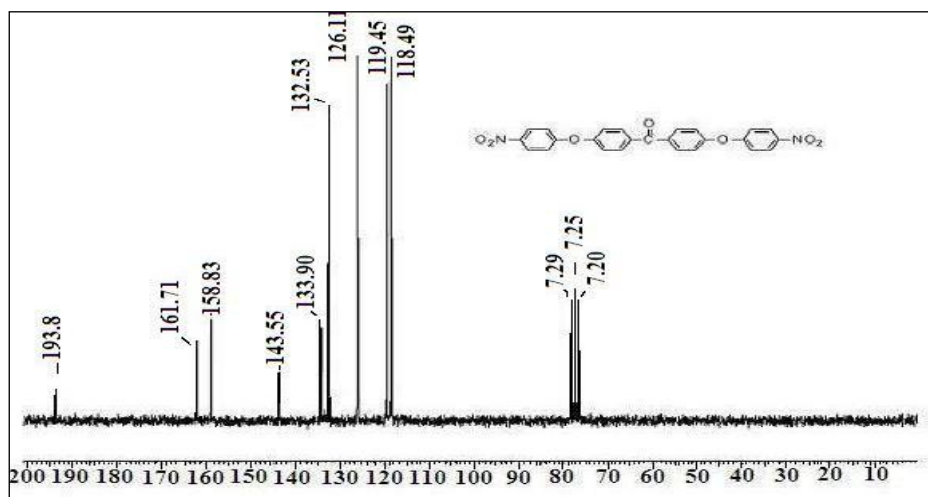


Fig.3 <sup>13</sup>C NMR spectrum of 4NPB (I)

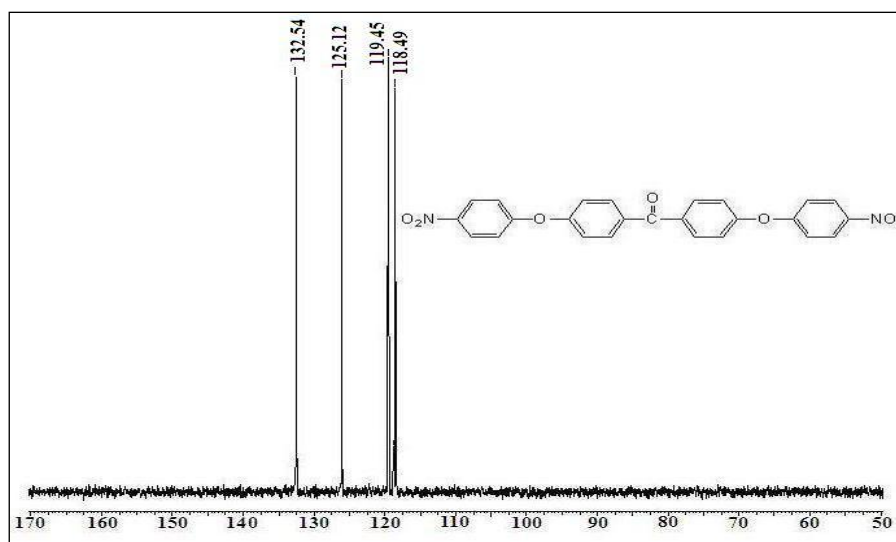


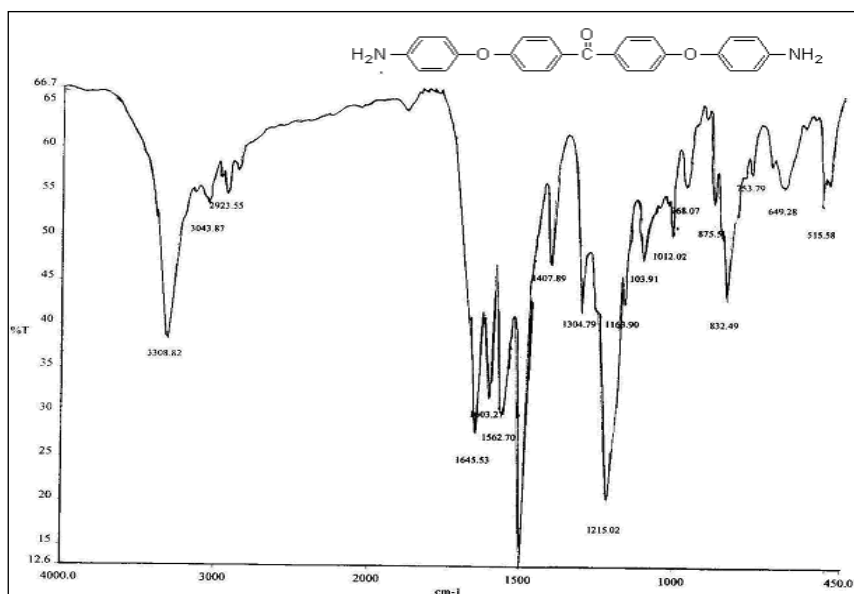
Fig.4 DEPT <sup>13</sup>C NMR spectrum of 4NPB (I)

**3.1.5. FT-IR spectrum of 4APB:**

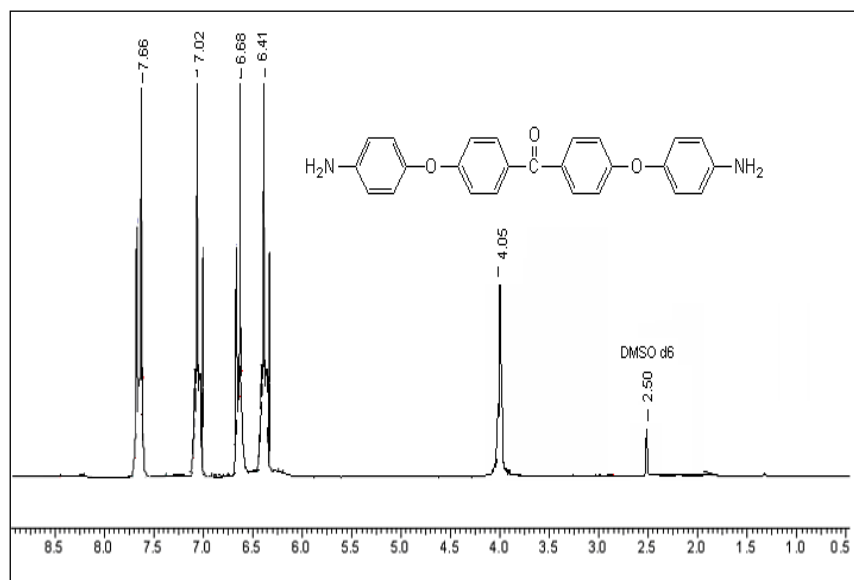
In the FT-IR spectrum of 4APB (**Fig.5**) the characteristic absorptions of the nitro group are absent and -NH stretching bands of the amino group appeared at  $3308\text{ cm}^{-1}$ . Strong absorptions at  $1645$  and  $1215\text{ cm}^{-1}$  correspond to CO (ketone) and -C-O-C- (ether).

**3.1.6.  $^1\text{H}$  NMR spectrum of 4APB:**

$^1\text{H}$  NMR spectrum of 4APB (**Fig.6**) exhibited the aromatic protons at 7.66 to 6.62 ppm. The signal for amino group appeared at 4.05 ppm.



**Fig.5** FT-IR spectrum (KBr) 4APB (II)



**Fig.6**  $^1\text{H}$  NMR spectrum of 4APB (II)

**3.1.7.  $^{13}\text{C}$  NMR spectrum of 4APB:**

$^{13}\text{C}$  NMR spectrum of 4APB (**Fig.7**) showed nine signals corresponding to nine different types of carbons of which CO carbon appeared at 195.5 ppm where as quaternary carbons appeared at 160.7, 141.3, 147.3 and 132.3 ppm and -CH carbons appeared at 130.1 117.3, 118.3 and 116.0 ppm.

**3.1.8. DEPT  $^{13}\text{C}$  NMR spectrum of 4APB:**

In the DEPT spectrum of 4APB (**Fig.8**), all the quaternary carbons were absent and -CH carbons appeared at upside 130.1 117.3, 118.3 and 116.0 ppm.

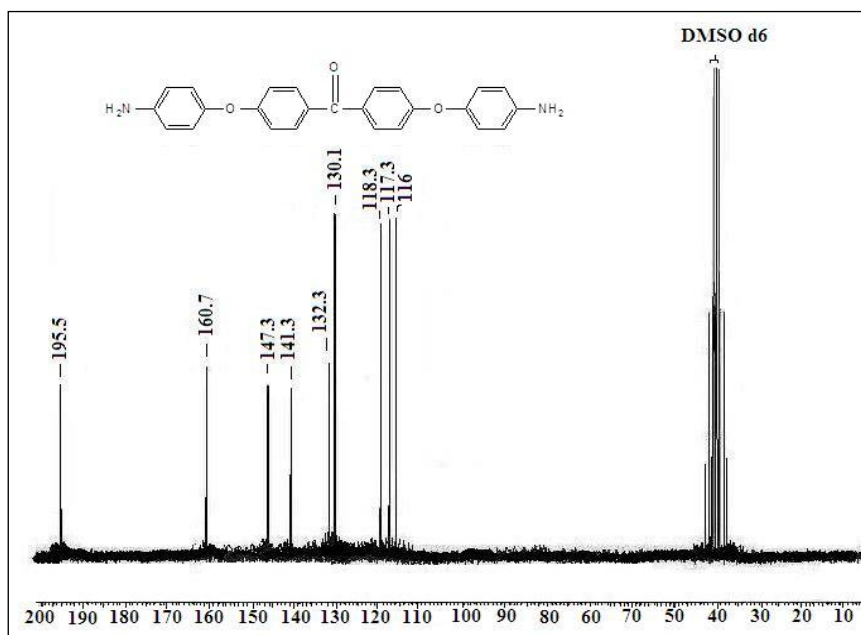


Fig.7  $^{13}\text{C}$  NMR spectrum of 4APB (II)

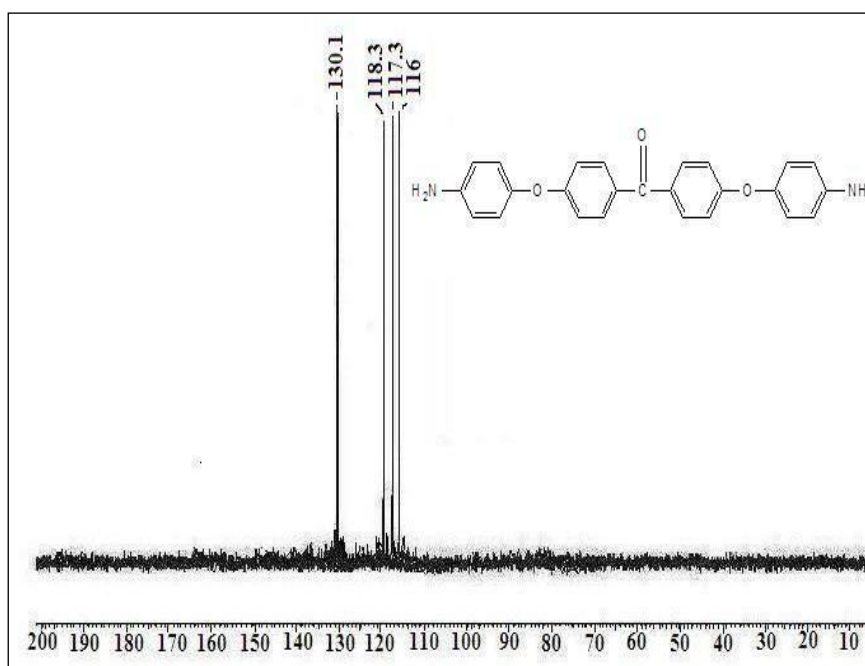


Fig.8 DEPT  $^{13}\text{C}$  NMR spectrum of 4APB (II)

### 3.1.9. FT-IR spectrum 4APPB:

FT-IR spectrum 4APPB (Fig.9) showed characteristic absorption bands at 3471, 3371 ( $-\text{NH}$  stretching) and  $1640\text{ cm}^{-1}$  ( $-\text{NH}$  deformation, characteristic of the  $\text{NH}_2$  group). The absorption peaks at 1647 (characteristic band of  $-\text{CO}-$  group) and 1238 1160 (characteristic of  $-\text{C}-\text{O}-\text{C}$  group). The bands observed at the 2924, 1495, 1598 and  $2852\text{ cm}^{-1}$  ( $-\text{CH}$  aliphatic), indicate pentadecyl group.

### 3.1.10. $^1\text{H}$ -NMR spectrum 4APPB:

$^1\text{H}$ -NMR spectrum 4APPB (Fig.10) supported the structure proposed. Aromatic protons of benzophenone unit showed signals in the range of 7.02 to 7.66 ppm. The signals at 6.37 to 6.53 ppm were assignable to protons of pentadecyl substituted aromatic ring.  $-(\text{C}_{15}\text{H}_{31})-$  whereas substituent pentadecyl group showed signals at 0.8 to 2.28 of which the signal {triplet} at 0.88 ppm is due to  $-\text{CH}_3$  protons and signals at 1.29 to 2.28 ppm is due to benzylic protons. Other  $(-\text{CH}_2-)_n$  protons appeared as broad peak because of overlapping. Proton in amide linkage showed signal at 3.9 ppm.



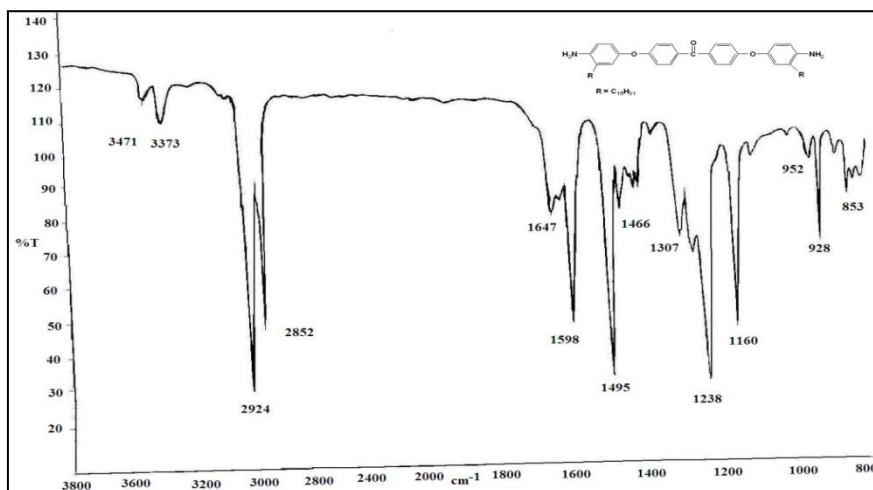


Fig.9 FT-IR spectrum 4APPB (III)

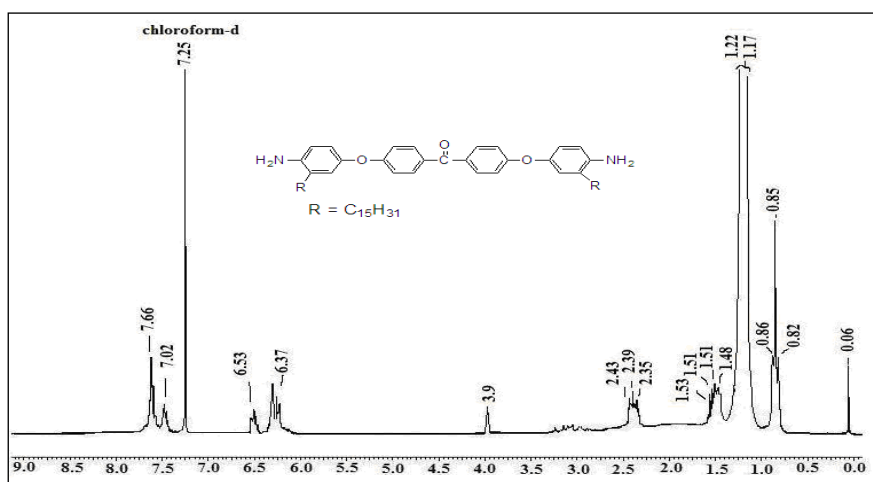


Fig.10 <sup>1</sup>H NMR spectrum of 4APPB (III)

### 3.1.11. <sup>13</sup>C NMR spectrum 4APPB:

<sup>13</sup>C NMR spectrum of 4APPB (Fig.11) showed eighteen CMR peaks of which eleven signals correspond to eleven types of carbonyl and aromatic carbons. Five (-CH) appeared signals at (128.94, 121.73, 119.07, 116.58 and 115.96 ppm) and five remaining carbon signals at (161.78, 161.17, 141.00, 132.17 and 131.51 ppm) were due to quaternary carbons. Carbonyl carbon appeared at 196.2 ppm, whereas aliphatic carbons due to pentadecyl substituents appeared in 14-32 ppm range.

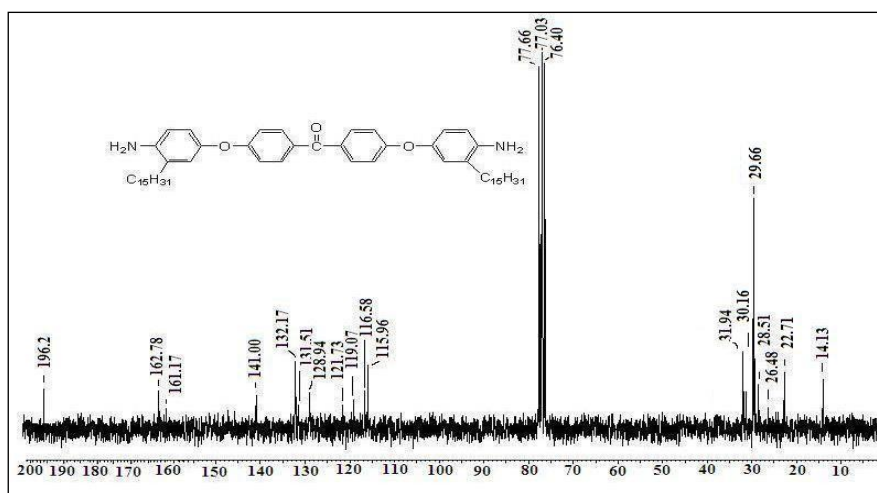


Fig.11 <sup>13</sup>C NMR spectrum of 4APPB (III)

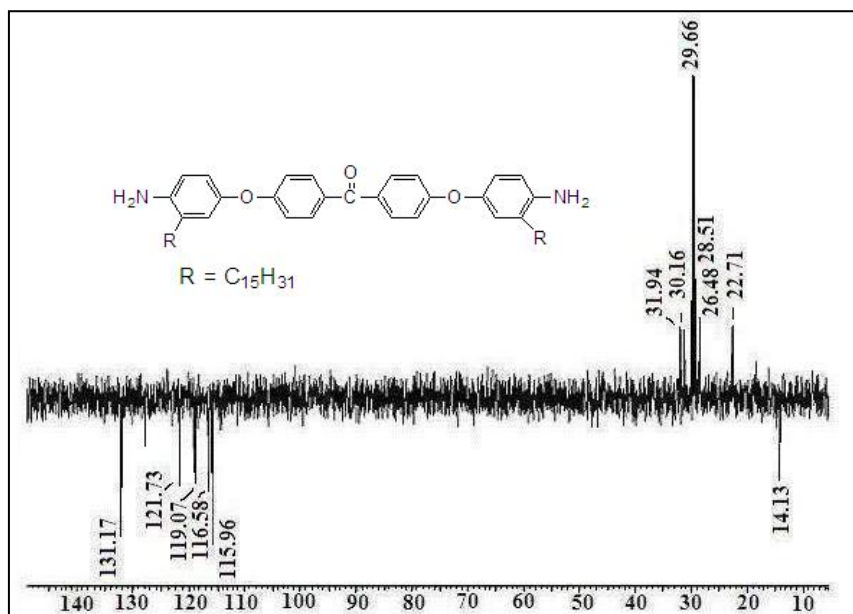


Fig.12 DEPT  $^{13}\text{C}$  NMR spectrum of 4APPB (III)

### 3.1.12. DEPT $^{13}\text{C}$ NMR spectrum of 4APPB:

DEPT  $^{13}\text{C}$  NMR spectrum 4APPB (Fig.12) also confirmed the structure of diamine monomer. The region of (114-165) ppm, showed only five methine (-CH) signals at (128.94, 121.73, 119.07, 116.58 and 115.96 ppm) as downside. The five remaining aromatic carbon signals (162.78, 161.17, 141.00, 132.17 and 131.51 ppm) due to quaternary carbons and -CO at 196.2 were absent. Among the carbon signals due to aliphatic pentadecyl substituents, -CH<sub>3</sub> was distinct in DEPT spectrum (14.13 ppm), where as benzylic -CH<sub>2</sub> appeared at 31.94 ppm. Signals at 30.16, 29.66, 28.51, 26.48 and 22.71 ppm were due to (-CH<sub>2</sub>)<sub>13</sub>, as upside.

### 3.2. Synthesis and characterization of the polymers:-

Aromatic polyamides and Co-polyamides PAIT-1 to PAIT-5 and PA15IT-1 to PA15IT-5 were prepared by the polycondensation of 4APB/4APPB with IPC/TPC using low temperature solution method in dry NMP and the synthetic route is shown in (Scheme. 3). These polymers were obtained in almost quantitative yield.

#### 3.2.1. FT-IR spectrum:

The IR spectra of PAIT-1 and PAIT-5, polymers showed absorption bands at 3300 (-NH stretching), a sharp band at 1660-1650 (amide I) and 1530-1520 cm<sup>-1</sup> (amide II). The absorption at 3039, (characteristics for aromatic stretching) and the sharp band at 1250 cm<sup>-1</sup> (C-O-C) also seen. The FT-IR spectrum of PA15IT-1 and PA15IT-5, Polyamides showed similar absorption bands pattern and 2937cm<sup>-1</sup> band correspond to (-CH stretching) due to pentadecyl substituent. Polymers showed the absorption peaks at 1235 cm<sup>-1</sup> corresponding to -C-O-C- vibration.

#### 3.2.2. Inherent viscosities:

The composition and data on inherent viscosities of polyamides and co-polyamides PAIT-1 to PAIT-5 and PA15IT-1 to PA15IT-5 are presented in (Table.1) respectively. The inherent viscosity of polyamides ranged from 0.20 to 0.75 dL/g, which imply the formation of moderate weight to high molecular weight polymers.

#### 3.2.3. Solubility:

The solubility of polyamides and copolyamides was qualitatively tested in a number of organic solvents and the results are summarized in (Table.2). Polymers showed good solubility in NMP (PAIT-1 to PAIT-5). Polyamides (PA15IT-1 to PA15IT-5) were soluble in polar aprotic solvents like DMSO, DMAc and solvents, like Pyridine, THF, DCM, CHCl<sub>3</sub> and meta-Cresol. Thus the C-15 alkyl group containing polyamides was more soluble in common organic solvent.

**Table-1** Synthesis of polyamides (PAIT-1 to PAIT-5) and (PA15IT-1 to PA-15IT-5) from 4APB / 4APPB and [IPC + TPC]

Polymer Code	Acid chloride (mol %)		Yield (%)	$\eta_{inh}^b$ (dL/g)
	IPC	TPC		
PAIT-1	100	00	96	0.34
PAIT-2	75	25	97	0.28
PAIT-3	50	50	97	0.20
PAIT-4	25	75	96	0.49
PAIT-5	00	100	97	0.57
PA15IT-1	100	00	96	0.67
PA15IT-2	75	25	96	0.75
PA15IT-3	50	50	96	0.59
PA15IT-4	25	75	96	0.46
PA15IT-5	00	100	96	0.64

a) Polymerization was carried out with 1mmol each of 4APB /4APPB and [IPC+TPC]  
 b) Measured at concentration of 0.5 g/dL in NMP at 30 ± 0.1°C.  
 c) 4'4'-bis-(4-amino phenoxy) benzophenone (4APB) (II) and 4, 4'-Bis (4"-amino phenoxy-3-pentadecyl) benzophenone; 4

**Table.2** Solubility of polyamides (PAIT-1 to PAIT-5) and (PA15IT-1 to PA15IT-5)

Solvent	Polymers									
	PAIT-1	PAIT-2	PAIT-3	PAIT-4	PAIT-5	PA15IT-1	PA15IT-2	PA15IT-3	PA15IT-4	PA15IT-5
NMP	++	++	++	++	++	++	++	++	++	++
DMAC	+-	+-	+-	+-	+-	+-	+-	+-	+-	+-
Conc. H <sub>2</sub> SO <sub>4</sub>	++	++	++	++	++	++	++	++	++	++
CHCl <sub>3</sub>	+-	+-	+-	+-	+-	++	+	+-	+-	--
m-cresol	+-	+-	+-	+-	+-	++	+	+	+	+
Pyridine	--	+-	--	--	+-	++	+	+	+	+
DMSO	--	+-	+-	+-	+-	--	--	--	--	--
DCM	--	+-	+-	--	+-	++	+	+-	+-	--
THF	++	+-	--	--	+-	++	++	+-	+-	+
DMF	+-	--	--	--	+-	+-	+-	--	--	--

Soluble at RT ++ Soluble on heating + Partly soluble +- Insoluble -

### 3.2.4. Thermogravimetric Analysis:

The thermogravimetric curves of polyamides are given in (Fig. 13) whereas, thermal data such, initial decomposition temperature ( $T_i$ ), 10% wt loss temperature ( $T_{10}$ ) and residual weight at 900 °C, is incorporated in (Table.3). The temperatures of 10% weight loss were above 420 °C. The stability of the polymer increased with the increase in content of terephthalic acid moiety. Polymers were stable up to 340 °C. Initial decomposition ( $T_i$ ) of polyamides (PA15IT-1 to PA15IT-5) was lower than polyamides (PAIT-1 to PAIT-5) due to presence of C-15 alkyl groups in polymer backbone

### 3.2.5. XRD pattern:

XRD pattern of the polymers PAIT-1 to PAIT-5 and PA15IT-1 to PA15IT-5 are presented in (Fig. 14). It is observed that crystallinity of the polymers increased as the percentage of TPC increased. The polymers obtained from 100 % TPC were more crystalline than 100 % IPC, as in former the close packing is possible.

**Table.3** TG curve polyamides (PAIT-1 to PAIT-5)<sup>a</sup> and (PA15IT-1 to PA15IT-5)<sup>a</sup> and DSC data.

Polymer Code	Temperature for various % Decomposition (°C)			Residual wt. (%) at 900 °C	$T_g$ (°C) <sup>c</sup>
	$T_i$ <sup>b</sup>	$T_{10}$ <sup>c</sup>	$T_{max}$ <sup>d</sup>		
PAIT-1	418	479	586	41	319
PAIT-2	350	433	498	55	320
PAIT-3	347	442	505	27	321
PAIT-4	355	448	525	35	332
PAIT-5	449	544	619	28	341
PA15IT-1	360	424	474	04	340
PA15IT-2	375	426	478	12	275
PA15IT-3	390	425	471	05	230
PA15IT-4	380	428	467	13	273

<b>PA15IT- 5</b>	385	455	490	54	341
a) Thermogravimetric analysis at a heating rate of 10 <sup>0</sup> C/min under nitrogen. b) Temperature at which initial loss of mass was observed. c) Temperature at which 10% weight loss was observed. d) Temperature at which “maximum rate of weight loss” was observed. e) Determined by DSC.					

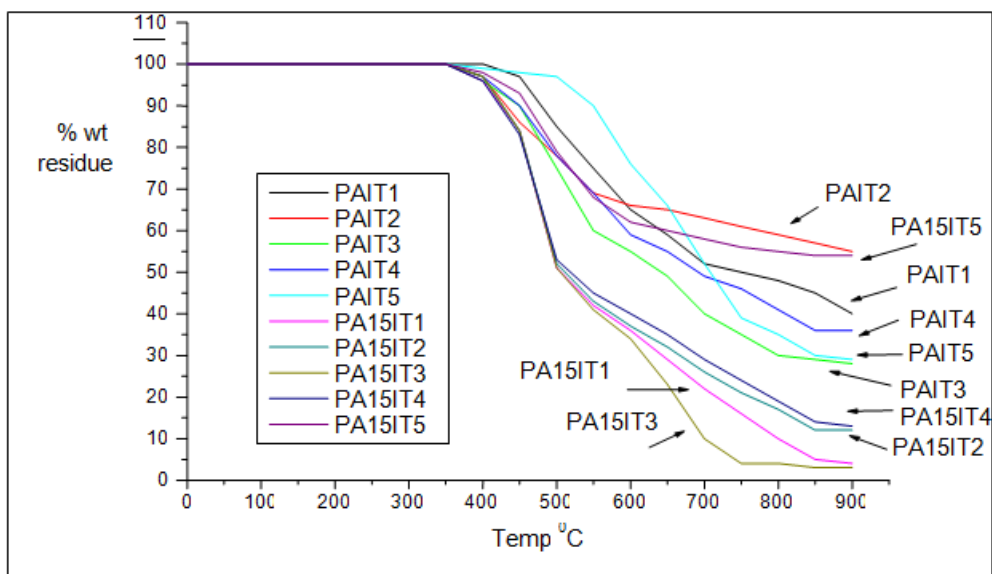


Fig. 13 TG curves of PAIT-1 to PAIT- 5 and PA15IT-1 to PA15IT-5

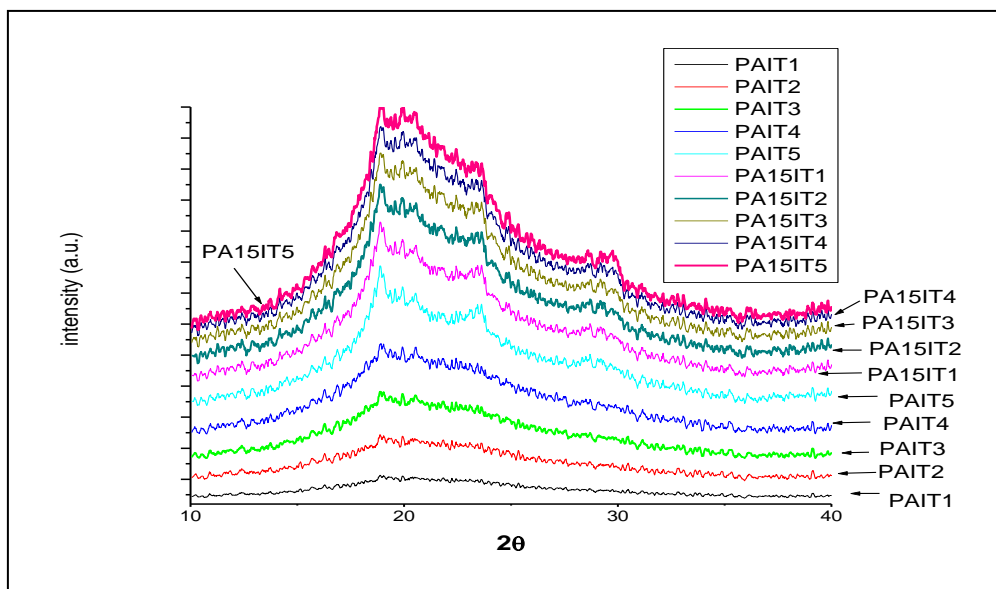


Fig. 14 XRD curves of PAIT-1 to PAIT-5 and PA15IT-1 to PA15IT-5

#### IV. Conclusion

Synthesis of **4APB** and **4APPB** was successfully accomplished and characterized by elemental analysis, FT-IR and NMR (<sup>1</sup>H and <sup>13</sup>C) techniques. A series of new polyamides (PAIT-1 to PAIT-5) containing aromatic ether ketone ether linkages and polyamides (PA15IT-1 to PA15IT-5) containing ether ketone ether linkages and pendent alkyl C-15 substituent were synthesized from **4APB/4APPB** and various mol % of isophthaloyl chloride (IPC)/terephthaloyl chloride (TPC) by using low temperature solution method. Polyamides were characterized by inherent viscosity, IR, solubility, DSC and TGA technique. Inherent viscosity values of polymers were in the range of 0.20 to 0.75 dL/g indicating built up of a moderately to high molecular weight. Some polyamides derived from **4APB** and **4APPB** were soluble in polar aprotic solvents because of presence of flexible ether ketone, ether and C-15 alkyl groups in polymer backbone. Thermal

stability of polymers was evaluated by TGA and all the polymers showed no weight loss below 340 °C. The XRD showed partly crystalline morphology for polymers. These new polymers are expected to find applications as gas separation membranes and engineering materials in aerospace and nuclear industries as high performance films, coatings etc.

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