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*Synthesis and Characterization of Novel Aromatic Polyamides Containing Pyridine Heterocyclic Ring and Schiff-Base

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Abstract

Six new aromatic polyamides **P_{ar}^1-P_{ar}^6** were prepared by direct Yamazaki's polycondensation reaction of 4-Phenylenediacrylic acid (PPDAA) with two new aromatic Schiff-Base diamine monomers 2,6-bis[(4-amino-2,6-dimethylphenyl)methylene]diaminopyridine (BADMDP), 1,4-bis(6-aminopyridin-2-ylimino)dimethylenebenzene (BAPIDB); and Phthalic acid (PA) with four new diamine monomers containing pyridine heterocyclic group and bearing bulky aromatic pendant groups in the 4-position of the pyridine ring 4-(4-amino-2,6-dimethylphenyl)-2,6-bis(4-aminophenyl)pyridine (ADPBAP), 4-(2-hydroxyphenyl)-2,6-bis(4-aminophenyl)Pyridine (HPBAP), 4-(4-chlorophenyl)-2,6-bis(4-aminophenyl)pyridine (CPBAP), and 4-(4-(2,6-bis(4-aminophenyl) pyridin-4-yl)phenyl)-2,6-bis(4-aminophenyl)pyridine (BAPPBAP) in the presence of $CaCl_2$ in Pyridine and Triphenyl phosphite (TPP) as condensing agents in N-methyl-2-Pyrolidinone (NMP) as solvent. 4-Phenylenediacrylic acid (PPDAA) was prepared by the condensation reaction of Terephthalaldehyde with Malonic acid in the presence of pyridine. The monomers were characterized by Fourier transform infrared (FTIR), and Nuclear magnetic resonance (^{1}H-NMR). The resulting polyamides were characterized by Fourier transform infrared (FTIR), and Nuclear magnetic resonance(^{1}H-NMR); and their physical properties including solubility, thermal stability and thermal behavior were studied as well. All of these new polymers show very good solubility in polar aprotic solvents and excellent thermal stability.

1. Introduction

Polyamides (PA's), are crystalline engineering thermoplastics exhibiting high performance characteristics such as high melting points, high mechanical strength, ductility, and excellent resistance to solvents[1] with recurring amide groups (*-CO-NH-*) as an integral part of the main polymer chain. The polyamides are generally divided into two groups:

a) Aliphatic polyamides (*Nylons*).
b) Aromatic polyamides (*Aramids*).

In 1974, the aliphatic and aromatic polyamides were given separate generic nomenclature by the U.S. Federal Trade Commission. The aliphatic polyamides are termed as Nylons and aromatic polyamides are termed as aramides[2]. Historically, The first synthetic polyamide, poly(3-benzoamide), an aromatic polyamide, was obtained by Harbordt in 1862, and the first aliphatic polyamide was reported in 1899 by Gabriel and Mass[3], where as high molecular weight polyamides were prepared in 1933 by Carothers[4]. Thermally stable polymers have been received extensive interest in recent decades because of increasing demands for high temperature polymers as the replacement for metals or ceramics in automotive, aerospace, and

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microelectronic industries[5-7]. Aromatic polyamides are certainly one of the most successful classes of high-temperature polymers, and have found extensive use in the aviation, automotive, and electronic industries[8]. It was well known that a large number of polymers containing heterocyclic ring in the main chain were resistant to high temperature[9].

These heterocyclic rings have polar groups, imparting an additional dipole moment to the molecule, and hence they can interact with each other and alter the properties of the polymers containing these groups[10]. On the other hand, Schiff-bases (also known as imine or azomethine), named after Hugo Schiff[11-13]. Schiff bases are an important class of organic compounds due to their flexibility[14]. Simple azomethine (-CH=N- groups) compounds are well known for their liquid crystalline properties. When the azomethine groups are incorporated into the polymer backbone, they exhibit good properties such as thermal stability, conductivity, fiber forming ability, liquid crystalline behavior, and non-linear optical properties[15].

A variety of methods for the synthesis of Schiff bases have been described. The classical synthetic route for synthesis of Schiff bases reported by Schiff involves condensation of primary amines with carbonyl compounds under azeotropic distillation[16,17]. Schiff base polymers are of considerable interest and have generally been produced by the polycondensation of diamines with various dicarbonyl compounds[18].

So in order to examine the presence of both heterocyclic, bulky pendant groups and Schiff base linkages in the polyamides backbone, the synthesis of diamine and tetraamine monomers containing pyridine heterocyclic groups and several kind of aromatic type pendant groups; and Schiff-base linkages were designed, with improved solubility and processability without too much sacrificing of their thermal and mechanical properties. It is well known that polyamides containing heterocyclic units in the main chain possess excellent thermal stabilities[19,20].

2. Experimental

2.1 Instruments

Fourier transform infrared (**FTIR**) spectra were recorded on a SHIMADZU-FTIR-8400S spectrometer (Japan) with KBr pellets in the optical range of 400–4000cm^{-1}. Nuclear magnetic resonance (**^{1}H-NMR)** spectra were registered using a Bruker, Ultra Shield 300Mhz, spectrometer (Switzerland) using DMSO-d_6 as a solvent. Thermogravimetry analysis (**TGA**) were performed on a Polymer laboratories co. England, Model PL-TG using a heating rate of 10°C/min in N_2 atmosphere within the temperature range of 30–700°C. The Solubility of the polymers was determined with (0.01*gm*) of a polymer in (2*ml*) of a solvent.

2.2 *Materials*

N-methyl-2-Pyrrolydinone (NMP) from (*ALFA-PRODUCTS*); Absolute Methanol, Acetic acid, Lithium Chloride (LiCl), Palladium on Charcoal10% (Pd/C10%), all from (*BDH/England*); Dichloromethane (CH_2Cl_2) from (*BIOSOLVE*); Ammonium acetate ($C_2H_7NO_2$), Malonic acid ($C_3H_4O_4$), all from (*CHEM-SUPPLY*); Hydrochloric acid (HCl), Salicylaldehyde ($C_7H_6O_2$), all from (*HiMedia*); Diethyl ether ($C_4H_{10}O$) from (*IGCC /England*); Calcium chloride ($CaCl_2$), 4-Chlorobenzaldehyde (ClC_6H_4CHO), 2,6-Diamino pyridine ($C_5H_7N_3$), Dimethyl Sulphoxide (DMSO), Glacial acetic acid, m-Cresol (C_7H_8O), N,N-Dimethylacetamide (C_4H_9NO), P-(Dimethylamino)benzaldehyde ($C_9H_{11}NO$), Phthalic acid ($C_8H_6O_4$), Piperidine ($C_5H_{11}N$), Pyridine (C_5H_5N), Terephthalaldehyde ($C_6H_4(CHO)_2$), Triphenyl phosphite (TPP) ($C_{18}H_{15}O_3P$), Tetrahydro- furane (THF) (C_4H_8O), all from (*MERCK*); Absolute Ethanol from (*Scharlab*

S.L); Acetone (C_3H_6O), P-nitroacetophenone ($O_2NC_6H_4COCH_3$), all from (*ALDRICH*); N,N-Dimethylformamide (DMF) (C_3H_7NO) from (*Sinopharm Chemical Reagent*); and Hydrazine monohydrate ($NH_2NH_2.H_2O$) from (*THOMAS-BAKER*).

2.3 Synthesis of Monomers :

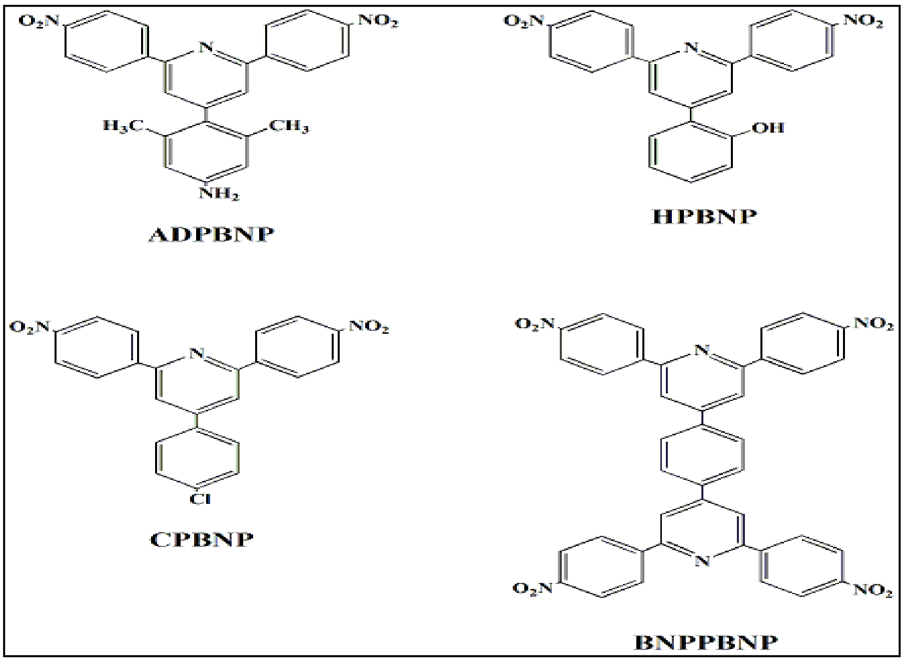
2.3.1 Synthesis of 4-(4-amino-2,6-dimethylphenyl)-2,6-bis(4-nitrophenyl) Pyridine [ADPBNP] :-

In a round-bottomed flask (150ml) equipped with a reflux condenser, a mixture of 4-(Dimethylamino)benzaldehyde (1.5gm, 10mmol), P-nitroacetophenone (P-NAP) (3.31gm, 20mmol), Ammonium acetate (7.5gm), and Glacial acetic acid (20ml) was refluxed at 140-142°C for 2h. Upon cooling, crystals separated, which were filtered and washed first with Acetic acid (50%) and then with cold Ethanol. These dark yellow crystals were recrystallized from absolute Ethanol, and then dried at 60°C under vacuum[21,22] to produce (3.608gm) (82%*wt*) of deep yellow crystals.
m.p 338-339°C.

The other dinitro and tetranitro compounds : 4-(2-hydroxyphenyl)-2,6-bis(4-nitrophenyl)Pyridine [**HPBNP**], 4-(4-chloro phenyl)-2,6-bis(4-nitro phenyl) pyridine [**CPBNP**], and 4-(4-(2,6-bis (4-nitrophenyl) pyridin-4-yl) phenyl)-2,6-bis (4-nitrophenyl) pyridine [**BNPPBNP**] were prepared by the same procedure as above using Salicylaldehyde, 4-Chlorobenzaldehyde, and Terephthalaldehyde, respectively, that are shown in (**Table 1**).

Table 1 : Synthesis of Monomers (HPBNP, CPBNP, BNPPBNP).

Monomers	**Substance**		**Weight gm**	**Yield (%wt)**	**Color**	**m.p/°C**
	aldehyde	**P-NAP**				
HPBNP	**1.22gm (10mmol)**	**3.31gm (20mmol)**	**3.35**	**81**	**deep yellow**	**341 decomposition**
CPBNP	**1.41gm (10mmol)**	**3.31gm (20mmol)**	**3.45**	**80**	**orange**	**50-56**
BNPPBNP	**1.34gm (10mmol)**	**6.62gm (40mmol)**	**5.73**	**80**	**light brown**	**360 decomposition**



Scheme 1 : Structure of ADPBNP, HPBNP, CPBNP, BNPPBNP.

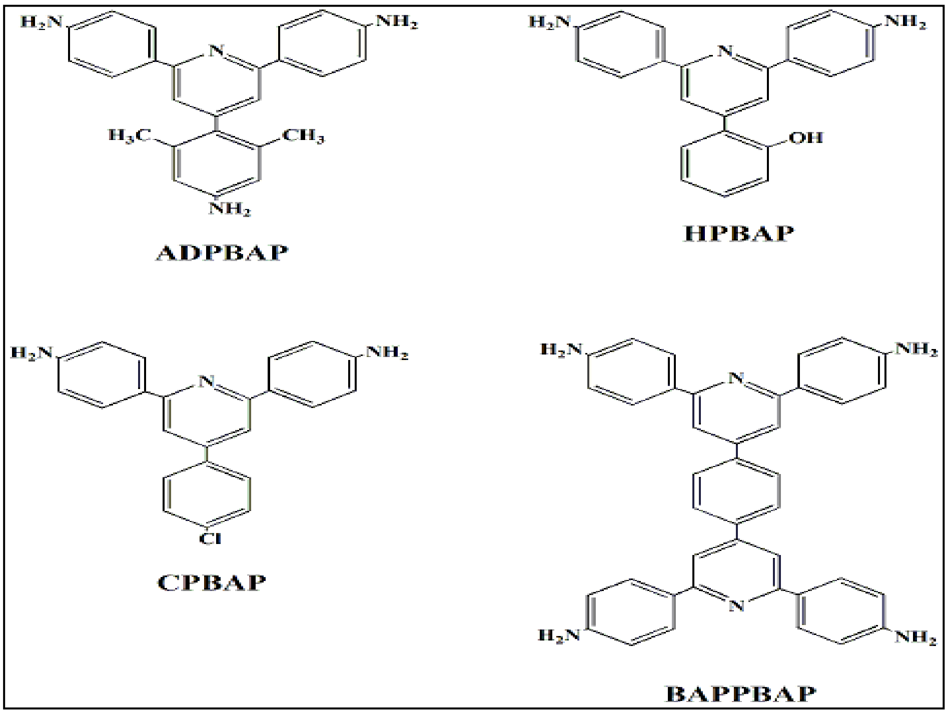
2.3.2 Synthesis of 4-(4-amino-2,6-dimethylphenyl)-2,6-bis(4-aminophenyl)pyridine [ADPBAP] :-

(2.64gm, 6mmol) of the ADPBNP, (0.2gm) of 10% Pd/C and (100ml) of ethanol were introduced into a three-necked flask to which (20ml) of hydrazine monohydrate was added dropwise over a period of 1h at 85°C. After the complete addition, the reaction was continued at reflux temperature for another 4h. To the suspension, (40ml) of THF was added to re-dissolve the precipitated product, and refluxing was continued for 1h. The mixture was filtered to remove the Pd-C, and the filtrate was poured into water. The product was filtered off, washed with hot water and dried in vacuum[23,24] to yielding (2gm) (88%wt) of yellow crystals. m.p 147-150°C.

The other diamino and tetra amino compounds : 4-(2-hydroxyphenyl)-2,6-bis(4-aminophenyl)Pyridine [**HPBAP**], 4-(4-chloro phenyl)-2,6-bis (4-amino phenyl) pyridine [**CPBAP**], and 4-(4-(2,6-bis(4-aminophenyl) pyridin-4-yl)phenyl)-2,6-bis(4-aminophenyl) pyridine [**BAPPBAP**] were reduced by the same procedure as above using HPBNP, CPBNP, and BNPPBNP, respectively, that are shown in (**Table 2**) .

Table 2 : Synthesis of Monomers (HPBAP, CPBAP, BAPPBAP).

Monomers Amino	Substance	Weight gm	Yield (%wt)	Color	m.p/°C
	Nitro				
HPBAP	2.5gm (6mmol)	1.82	86	brown	200 decomposition
CPBAP	2.6gm (6mmol)	2	89	deep yellow	136-140
BAPPBAP	4.3gm (6mmol)	3.2	89	light yellow	260 decomposition



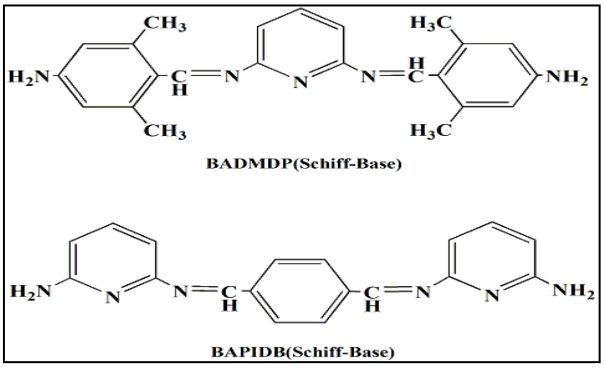
Scheme 2 : Structure of ADPBAP, HPBAP, CPBAP, BAPPBAP.

2.3.3 Synthesis of 2,6-Bis [(4-amino-2,6-dimethyl phenyl) methylene] diaminopyridine [BADMDP Schiff-Base]:-

This monomer was prepared by the condensation of 4-(Dimethylamino)- benzaldehyde (3gm, 20mmol) and 2,6-diaminopyridine (1.1gm, 10mmol) in 15ml of methanol, by boiling the mixture under reflux at 120°C for 3h. The precipitated was filtered and recrystallized from methanol and dried in a *vacuum* desiccators[25] to yielding 2.93gm (79%*wt*) of light green crystals. m.p 79-83°C.

2.3.4 Synthesis of 1,4-Bis (6-aminopyridin-2-ylimino)dimethylene benzene [BAPIDB Schiff-Base] :-

This monomer was prepared by the condensation of Terephthalaldehyde (1.35gm, 10mmol) and 2,6-diaminopyridine (2.18gm, 20mmol) by the same procedure as above to yielding (3.1gm) (98%*wt*) of white crystals.
m.p 71-74°C

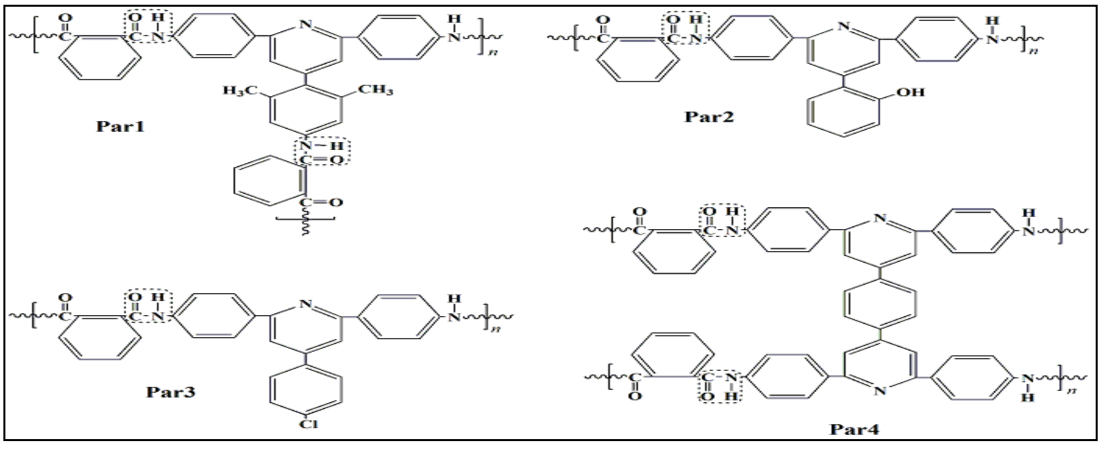


Scheme 3 : Structure of BADMDP(Schiff-Base), BAPIDB(Schiff-Base).

2.4 Synthesis of Polyamides :

2.4.1 Synthesis of [P_{ar}^{1} - P_{ar}^{4}] :-

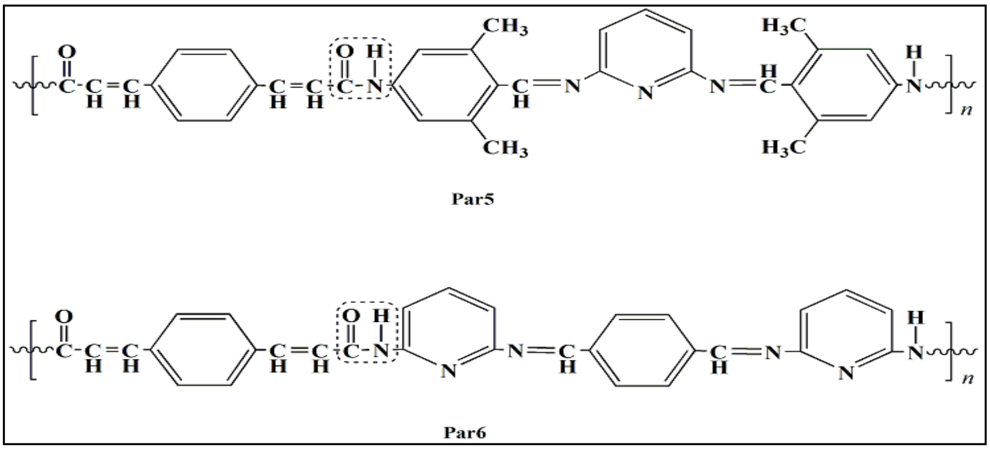
A 500ml four neck round flask equipped with a nitrogen inlet, a thermometer, and a mechanical stirrer was charged with (5 or 10)mmol of Phthalic acid (**PA**), (5mmol) of ***Heterocyclic*** diamine monomer, that shown in (*Table* **3**), (3gm) of $CaCl_2$, (10ml) of Pyridine, (1ml) of TPP, and (5ml) of NMP. The mixture was heated under nitrogen to 110°C and stirred for 3h. The viscous solution was then cooled down and precipitated into (50ml) of methanol. The stringy polymer was washed thoroughly with hot water and methanol, collected by filtration, and dried at 100°C under *vacuum*[26-28].



Scheme 4 : Repeating unit of P_{ar}^{1}, P_{ar}^{2}, P_{ar}^{3}, P_{ar}^{4}.

2.4.2 Synthesis of [P_{ar}^5 - P_{ar}^6] :-

A flask equipped with a mechanical stirrer and a condenser was charged with a mixture of **PPDAA** (5mmol) and ***Schiff-Base*** diamine monomer (5mmol), that shown in (**Table 3**), Pyridine (10ml), Lithium Chloride (1.4gm), and NMP (10ml). The mixture, blanketed by nitrogen, was stirred and heated to 120°C. TPP (5ml) was then added to the solution, and the reaction proceeded for 4h. The viscous final solution was poured into (100ml) of methanol, and the collected polymer was washed thoroughly with hot water and methanol. The polymer was dried in a *vacuum oven* at 110°C overnight[29].



Scheme 5 : Repeating unit of P_{ar}^5, P_{ar}^6.

Table 3: Synthesis of Polyamides [P_{ar}^1 - P_{ar}^6]

Polyamides	Monomers		diacid	diamine	Yield (% wt)	Color
	diacid	diamine	gm/mmol	gm/5mmol		
P_{ar}^1	PA	ADPBAP	1.66 (10mmol)	1.9	81	light brown
P_{ar}^2	PA	HPBAP	0.83 (5mmol)	1.765	83	deep brown
P_{ar}^3	PA	CPBAP	0.83 (5mmol)	1.85	98	light brown
P_{ar}^4	PA	BAPPBAP	1.66 (10mmol)	2.98	93	very-light brown
P_{ar}^5	PPDAA	BADMDP	1.09 (5mmol)	1.855	99	light beige
P_{ar}^6	PPDAA	BAPIDB	1.09 (5mmol)	1.58	80	white

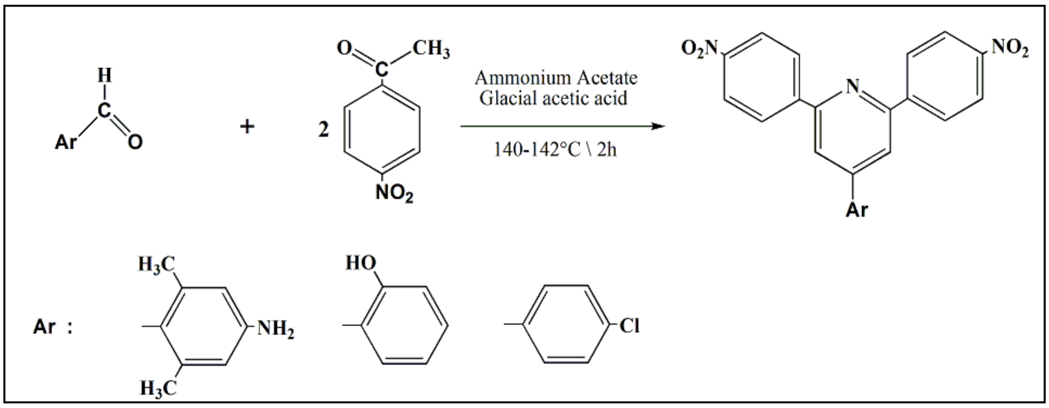
3. Results and Discussion

3.1 Synthesis of Monomers :-

3.1.1 Synthesis of Heterocyclic di and tetra Nitro Monomers [ADPBNP, HPBNP, CPBNP, and BNPPBNP] :-

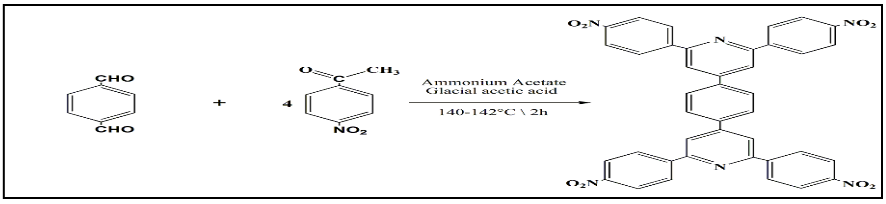
There are several methods for preparation of the pyridine ring. Modified Chichibabin method is one of the best methods for the preparation of a pyridine ring[30], which offers advantages such as good yield, available starting material and potential for introducing different substituent's in the pyridine ring.

ADPBNP, **HPBNP**, and **CPBNP** monomers are prepared by the condensation of one molecule of 4-(Dimethylamino) benzaldehyde, Salicylaldehyde, and 4-Chlorobenzaldehyde, respectively with two molecules of P-nitroacetophenone in the presence of ammonium acetate and glacial acetic acid at 140-142°C for 2h. These monomers were characterized by FTIR.



Scheme 6 : Synthesis of ADPBNP, HPBNP, CPBNP monomers.

BNPPBNP monomer is prepared by the condensation of one molecule of Terephthalaldehyde with four molecules of P-nitroacetophenone in the presence of ammonium acetate and glacial acetic acid at 140-142°C for 2h. This monomer was characterized by FTIR.



Scheme 7 : Synthesis of BNPPBNP monomer.

Characterization of [ADPBNP] :-

The *FTIR* spectrum is shown in (**Figure 1**) which indicated absorption bands at (3600cm^{-1}) to (–NH$_2$ group), (1434cm^{-1}), (1342cm^{-1}) to (–NO$_2$) asymmetric and symmetric stretching, respectively, (3050cm^{-1}) to (aromatic –CH stretching), (2800cm^{-1}) to (aliphatic –CH stretching), absorption bands around (1670–1650cm^{-1}) show the presence of the aromatic rings, and (1589–1519 cm^{-1}) to heteroaromatic ring (C=N).

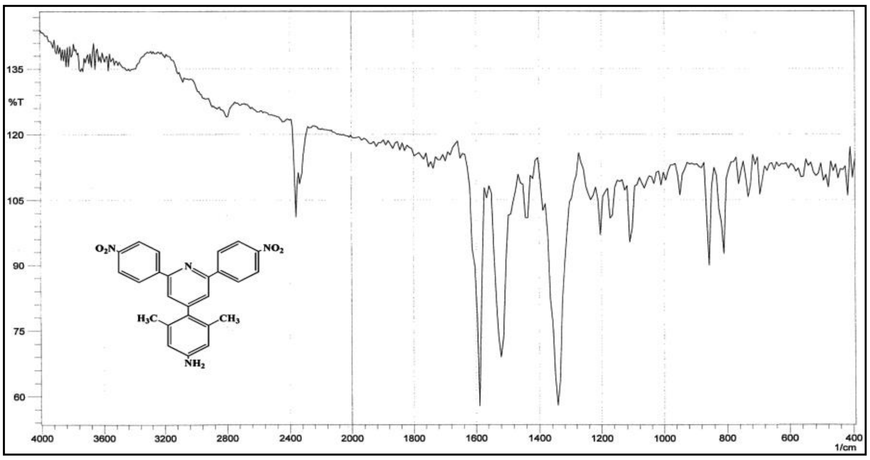


Figure 1 : FTIR spectrum of ADPBNP monomer.

Characterization of [HPBNP] :-

The *FTIR* spectrum is shown in (**Figure 2**) which indicated absorption band at (3386cm^{-1}) to (–OH group), (3150cm^{-1}) to (aromatic –CH stretching), (1404cm^{-1}), (1342cm^{-1}) to (–NO$_2$) asymmetric and symmetric stretching, respectively, absorption bands around (1681–1666cm^{-1}) show the presence of the aromatic ring, and (1596–1527cm^{-1}) to heteroaromatic ring (C=N).

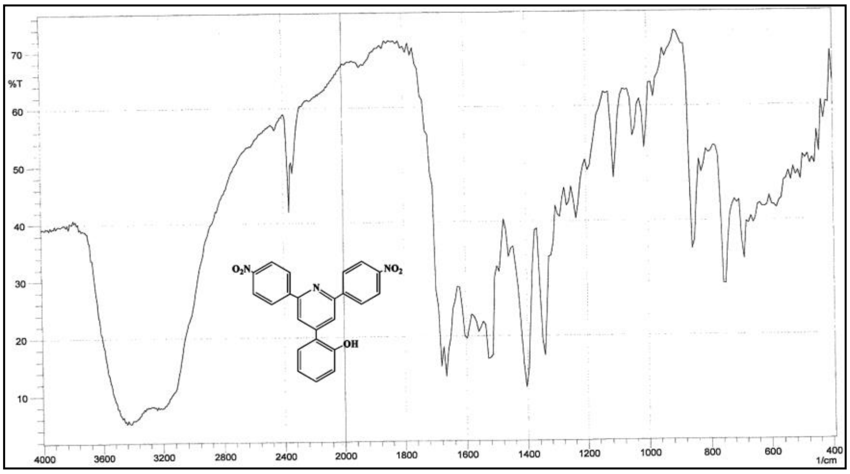


Figure 2 : FTIR spectrum of HPBNP monomer.

Characterization of [CPBNP] :-

The *FTIR* spectrum is shown in (**Figure 3**) which indicated absorption band at (1488cm^{-1}), (1319cm^{-1}) to (–NO$_2$) asymmetric and symmetric stretching, respectively, absorption bands around (1689–1666cm^{-1}) show the presence of the aromatic ring, (1596–1519cm^{-1}) to heteroaromatic ring (C=N), and (817cm^{-1}) to (C–Cl).

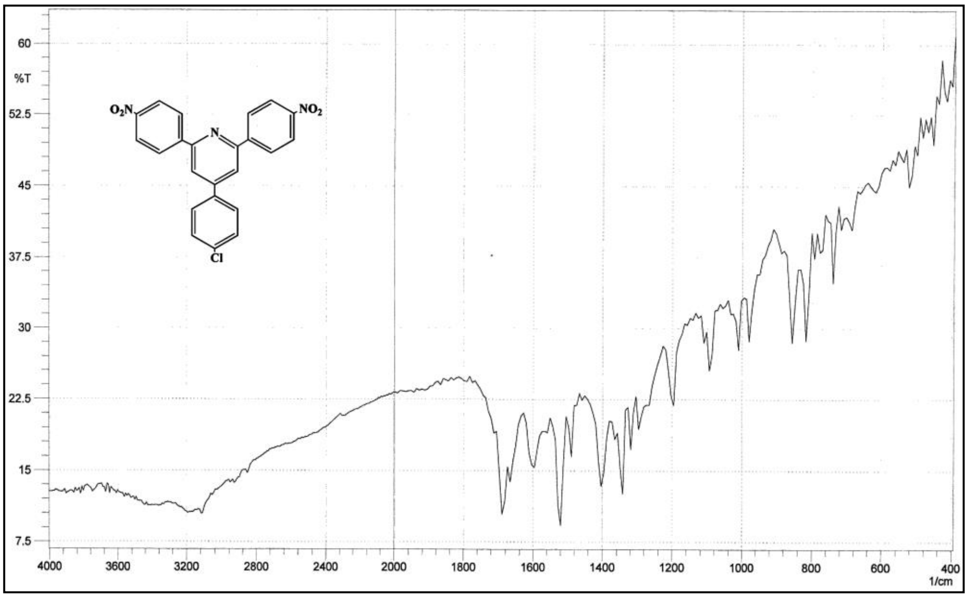


Figure 3 : FTIR spectrum of CPBNP monomer.

Characterization of [BNPPBNP] :-

The *FTIR* spectrum is shown in (**Figure 4**) which indicated absorption bands at (1427cm^{-1}), (1350cm^{-1}) to (–NO_2) asymmetric and symmetric stretching, respectively, (3170cm^{-1}) to (aromatic –CH stretching), absorption bands around (1690–1604cm^{-1}) show the presence of the aromatic ring, and (1590–1504 cm^{-1}) to heteroaromatic ring (C=N).

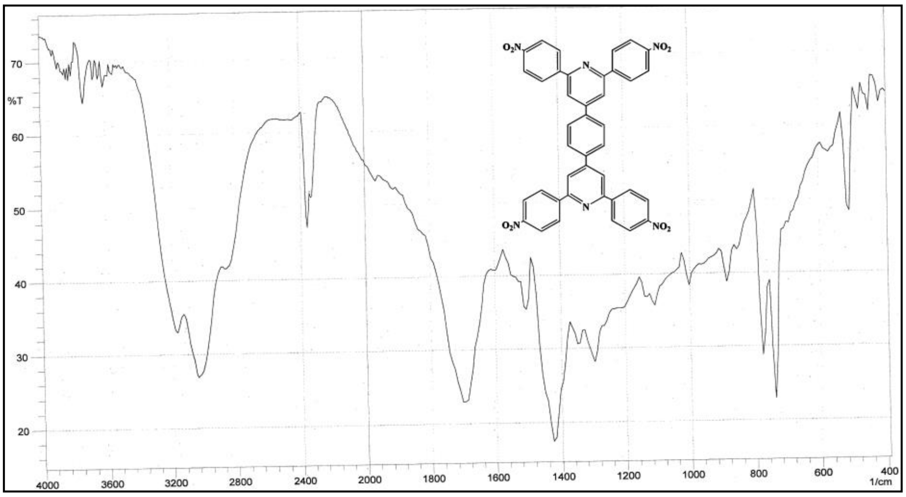
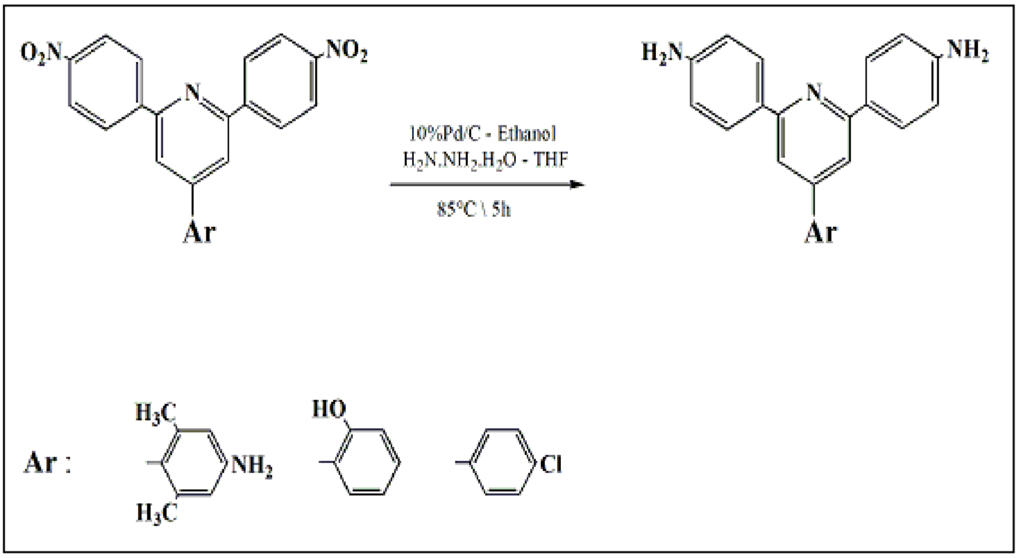


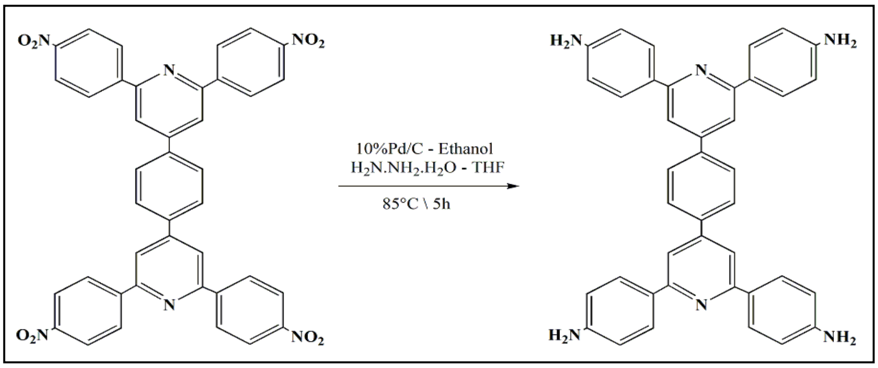
Figure 4 : FTIR spectrum of BNPPBNP monomer.

3.1.2 Synthesis of Heterocyclic di and tetra Amino Monomers [ADPBAP, HPBAP, CPBAP, and BAPPBAP] :-

The catalytic hydrogenation of nitro group in the ADPBNP, HPBNP, CPBNP, and BNPPBNP to amino compound ADPBAP, HPBAP, CPBAP, and BAPPBAP, respectively was accomplished by using hydrazine monohydrate and catalytic amount of Pd/C as reducing agent[31] at 85°C for 5h. These monomers were characterized by *FTIR* and *^1H NMR* spectra.



Scheme 8 : Synthesis of ADPBAP, HPBAP, CPBAP monomers.



Scheme 9 : Synthesis of BAPPBAP monomer.

Characterization of Heterocyclic di and tetra Amino Monomers:-

In the FTIR spectra of (ADPBAP, HPBAP, CPBAP, and BAPPBAP) (**Figure 5-8**), the characteristic absorptions of the nitro group disappeared and (–NH) stretching absorption bands of the amino group appeared broad at (3348cm^{-1}), (3363cm^{-1}), (3348cm^{-1}), and (3350cm^{-1}), respectively.

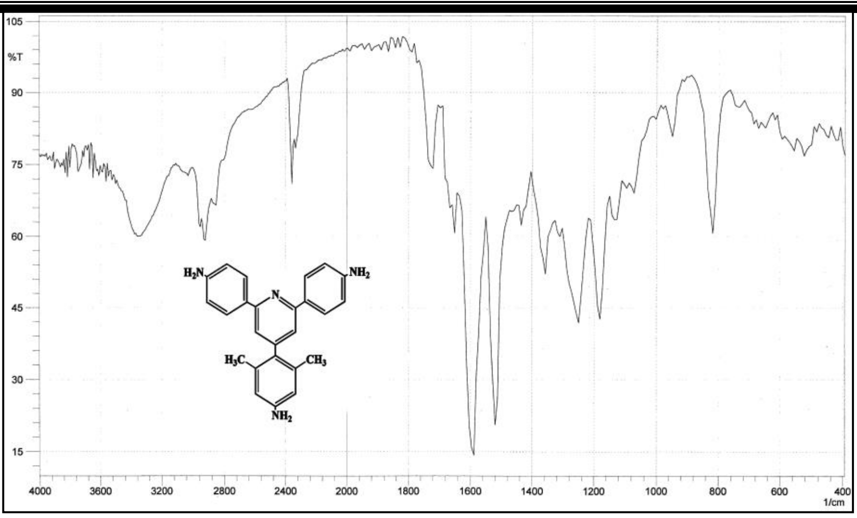


Figure 5 : FTIR spectrum of ADPBAP monomer.

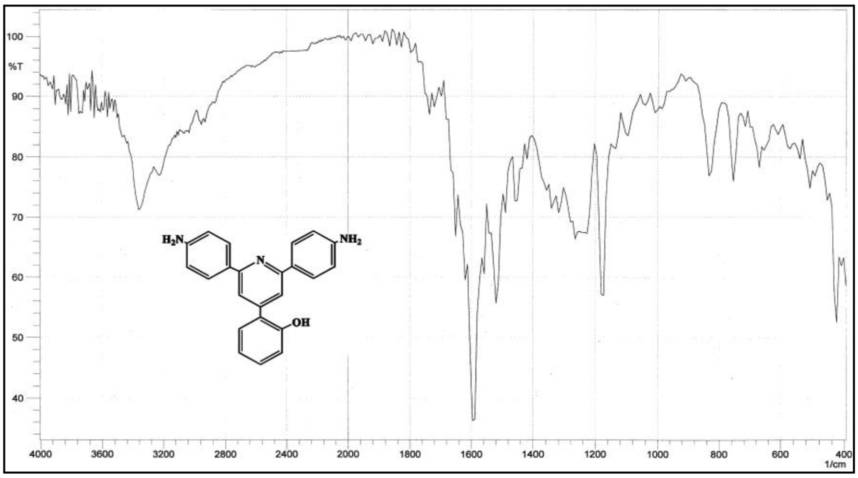


Figure 6 : FTIR spectrum of HPBAP monomer.

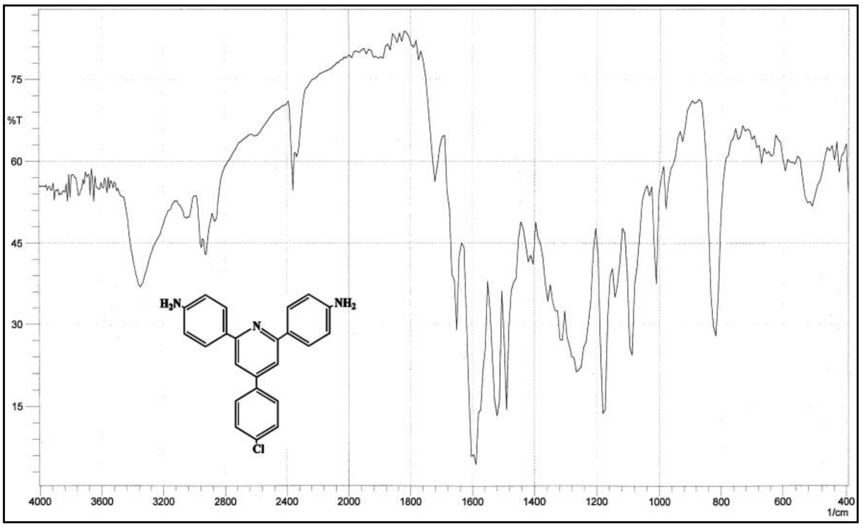


Figure 7 : FTIR spectrum of CPBAP monomer.

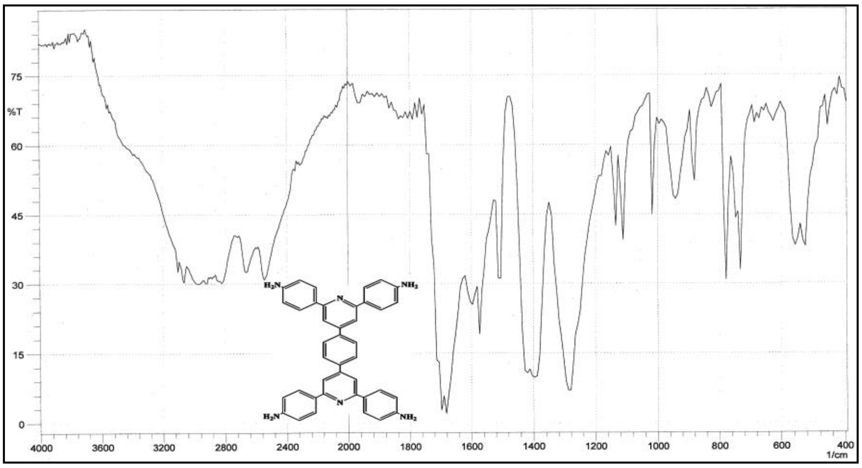


Figure 8 : FTIR spectrum of BAPPBAP monomer.

^{1}**H-NMR** spectrum of ADPBAP in (**Figure 9**) shows a singlet at (2.246 δ ppm) to (6H, CH_3), a singlet at (3.737 δ ppm) to (6H, NH_2), and a multiplet at (6.833-7.834 δ ppm) to (12H, Phenyl and hetero rings).

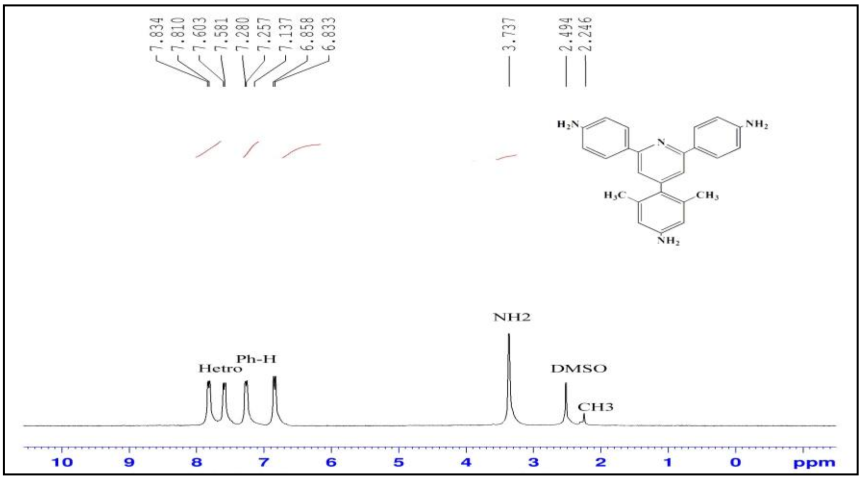


Figure 9 : ^{1}H NMR spectrum of (ADPBAP) monomer.

^{1}H-NMR spectrum of CPBAP in (Figure 10) shows a singlet at (3.747 δ ppm) to (4H, NH_2), and a multiplet at (6.047-7.993 δ ppm) to (14H, Phenyl and hetero rings).

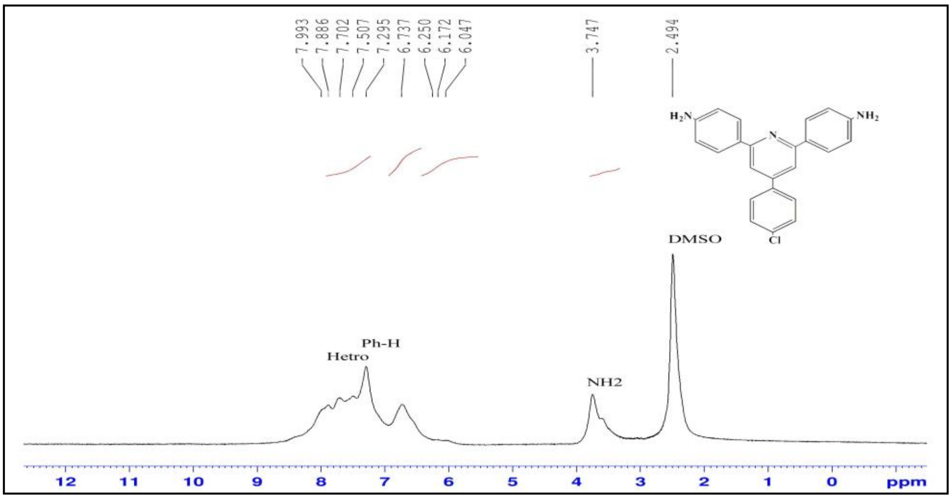


Figure 10 : ^{1}H NMR spectrum of (CPBAP) monomer.

^{1}H-NMR spectrum of BAPPBAP in (**Figure 11**) shows a singlet at (3.760 δ ppm) to (8H, NH_2), and a multiplet at (6.788-7.993 δ ppm) to (24H, Phenyl and hetero rings).

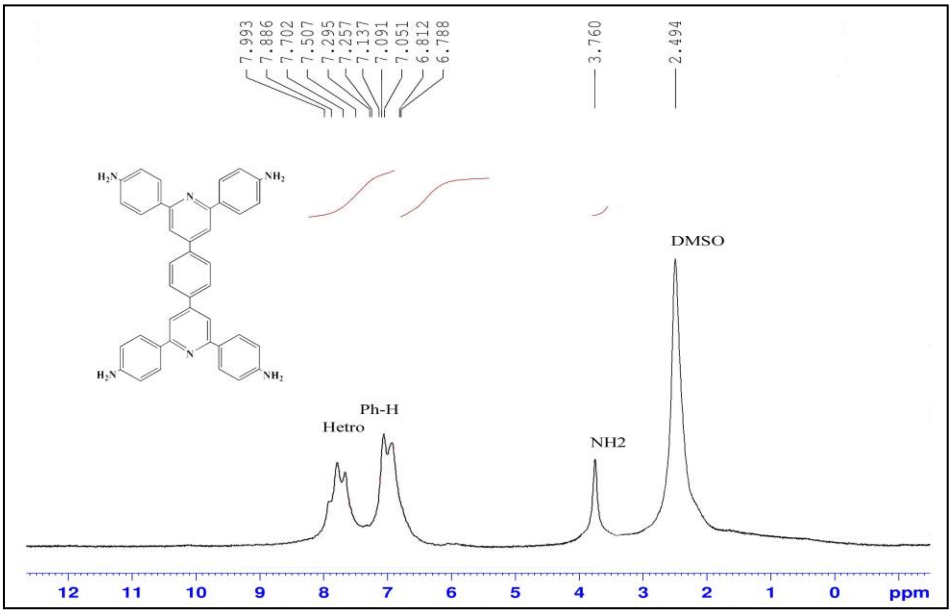
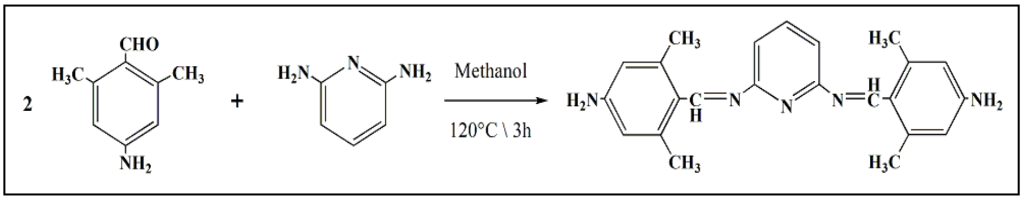


Figure 11 : ^{1}H NMR spectrum of (BAPPBAP) monomer.

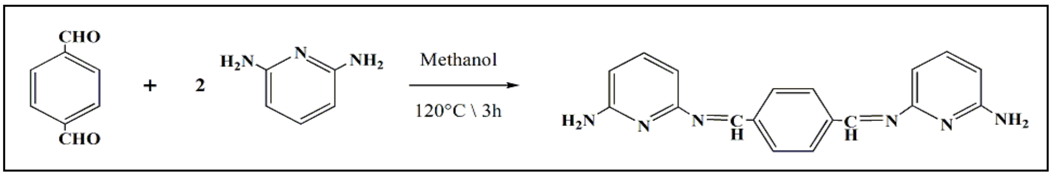
3.1.3 Synthesis of [BADMDP , BAPIDB] "Schiff – Base" monomers :-

BADMDP is prepared by the condensation of two molecules of 4-(Dimethylamino)-benzaldehyde with one molecule of 2,6-diaminopyridine in the presence of Methanol at 120°C for 3h. This monomer was characterized by *FTIR* and ^{1}*H NMR* spectra.



Scheme 10 : Synthesis of BADMDP Schiff-Base monomer.

BAPIDB is prepared by the condensation of one molecule of Terephthalaldehyde with two molecules of 2,6-diaminopyridine in the presence of Methanol at 120°C for 3h. This monomer was characterized by *FTIR* spectrum.



Scheme 11 : Synthesis of BAPIDB Schiff-Base monomer.

Characterization of BADMDP and BAPIDB Schiff-Base Monomers :-

The *FTIR* spectrum is shown in (**Figure 12**) which indicated absorption bands at (3625cm^{-1}) to (–NH$_2$ group), (3100cm^{-1}) to (aromatic –CH stretching), (2916cm^{-1}) to (aliphatic –CH stretching), absorption bands around (1604–1589cm^{-1}) show the presence of the aromatic ring, and (1550–1535cm^{-1}) to heteroaromatic ring (C=N).

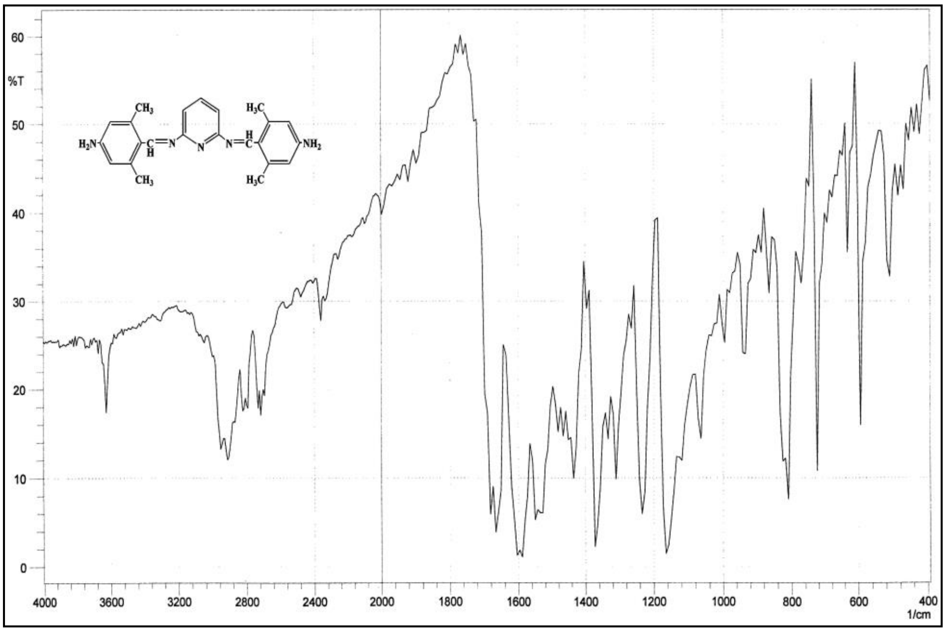


Figure 12 : FTIR spectrum of BADMDP Schiff-Base monomer.

^{1}H-NMR spectrum of BADMDP *Schiff-Base* in (**Figure 13**) shows a singlet at (2.208 δ ppm) to (12H, CH$_3$), a singlet at (3.723 δ ppm) to (4H, NH$_2$), multiplet at (6.664 - 7.721 δ ppm) to (7H, Phenyl and hetero rings) and a singlet at (9.697 δ ppm) to (2H, CH=N Schiff-Base group).

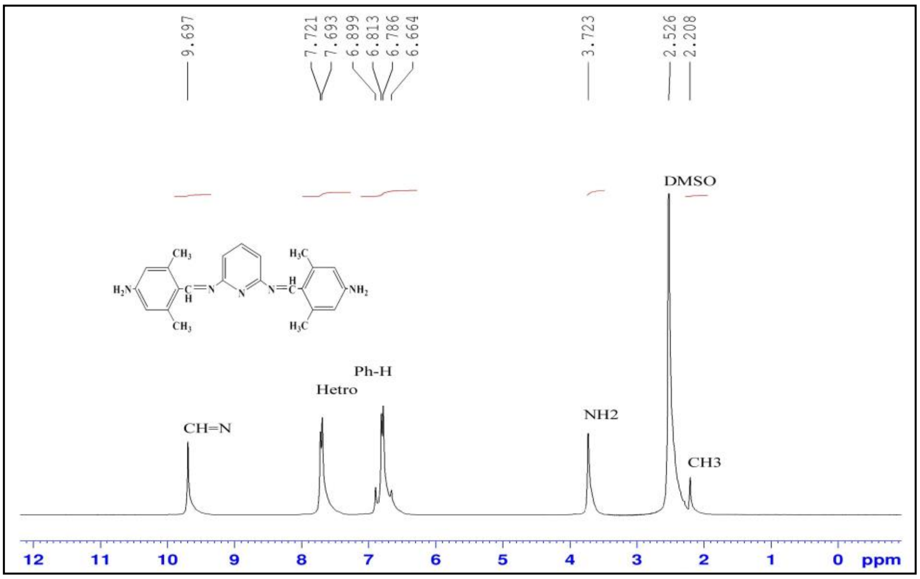


Figure 13 : ^{1}H NMR spectrum of (BADMDP Schiff-Base) monomer.

The FTIR spectrum of (BAPIDB *Schiff-Base*) is shown in (**Figure 14**) which indicated absorption bands at (3625cm^{-1}) to (–NH$_2$ group), (3070cm^{-1}) to (aromatic –CH stretching), (2916cm^{-1}) to (aliphatic –CH stretching), absorption bands around (1610–1542cm^{-1}) show the presence of the aromatic ring, and (1519–1504cm^{-1}) to heteroaromatic ring (C=N).

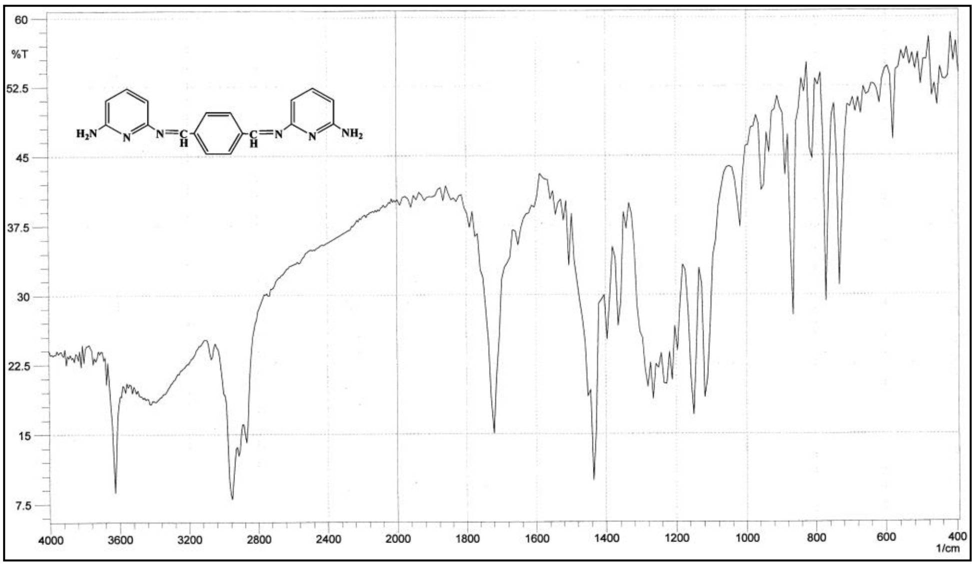


Figure 14 : FTIR spectrum of BAPIDB Schiff-Base monomer.

3.2 Synthesis of Polyamides :-

Generally, it is known that one of the successful approaches to increase the solubility and processability without sacrificing high thermal stability is the introduction of bulky and unsymmetrical groups, flexible bonds, large pendent or polar substituents into the polymer backbone[32].

The attachment of flexible side chains has been drawing particular interest in polyamide synthesis, because it increases not only solubility but also maintain (Tg) through controlled segmental mobility.

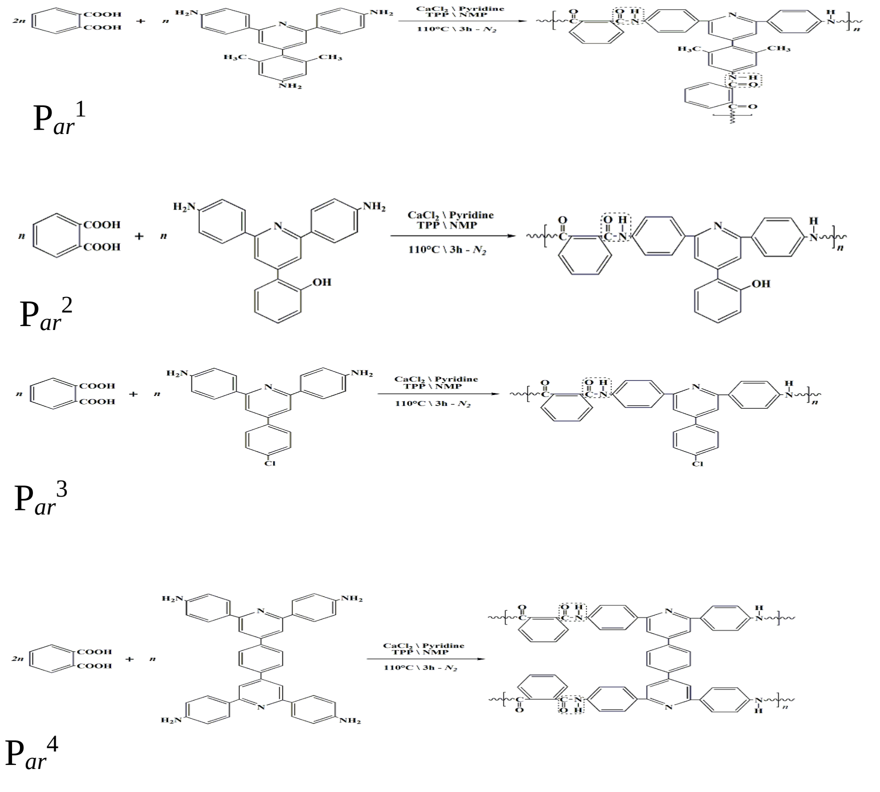
Phosphorylation polycondensation reaction has been applied extensively to polyamides synthesis since 1975, when Yamazaki, Matsumoto and Higashi reported this reaction. This technique employs (TPP) as condensing agents to synthesize polyamides directly from aromatic diamines and aromatic dicarboxylic acids. The reaction proceeds through formation of N-phosphonium salts of pyridine, followed by aminolysis. The advantages of direct polycondensation method over low temperature solution method are :

(a) the polymerization is carried out at moderate temperature without removing the side product.**(b)** avoids tedious step of acid chloride preparation and it’s storage.

In the present investigation, series of new aromatic polyamides were synthesized by the reaction of stoichiometric quantities of new aromatic di and tetra amines with commercially available diacids by Yamazaki’s phosphorylation method using TPP as condensing agent. The effect of introduction of pyridine heterocyclic ring, Schiff-Base linkages, aromatic groups, and structure of various diacids into polymer backbone was studied in detail.

3.2.1 Synthesis of [P_{ar}^1 - P_{ar}^4] :-

In this section, we synthesized new **four** processable polyamides [$\mathbf{P_{ar}^1}$ - $\mathbf{P_{ar}^4}$] with enhanced thermal stabilities from **four** new different aromatic di and tetra amine monomers **[ADPBAP**, **HPBAP**, **CPBAP**, and **BAPPBAP]**, respectively containing ***pyridine heterocyclic*** groups and bearing bulky aromatic pendant groups in the 4-position of the pyridine ring with **Phthalic acid** in the presence of $CaCl_2$ in Pyridine, and TPP as condensing agents in NMP as solvent. These polyamides were characterized by *FTIR* and *^{1}H-NMR spectra*.



P_{ar}^1

P_{ar}^2

P_{ar}^3

P_{ar}^4

Scheme 12 : Synthesis of P_{ar}^1- P_{ar}^4.

Characterization of [P_{ar}^1 - P_{ar}^4] :-

The *FTIR* spectrum of (P_{ar}^1) showed (**Figure 15**) absorption bands at (3363cm^{-1}) to (–NH stretching), (3130cm^{-1}) to (aromatic –CH stretching), (2900cm^{-1}) to (aliphatic –CH stretching), the sharp bands at (1743–1720)cm^{-1} to (C=O amide), (1658–1550)cm^{-1} to (C=C) ring, and (1596–1519)cm^{-1} to (C=N).

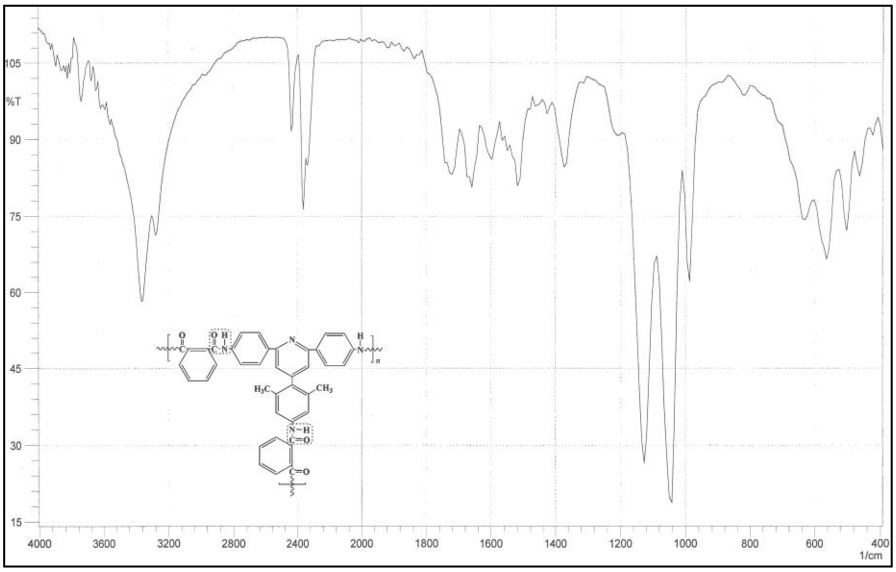


Figure 15 : FTIR spectrum of P_{ar}^1.

The *FTIR* spectrum of (P_{ar}^2) showed (**Figure 16**) absorption bands at (3394cm^{-1}) to (–NH stretching), (3350cm^{-1}) to (–OH group), (3062cm^{-1}) to (aromatic –CH stretching), the sharp bands at (1720–1650)cm^{-1} to (C=O amide), (1635–1558)cm^{-1} to (C=C) ring, and (1596–1512)cm^{-1} to (C=N).

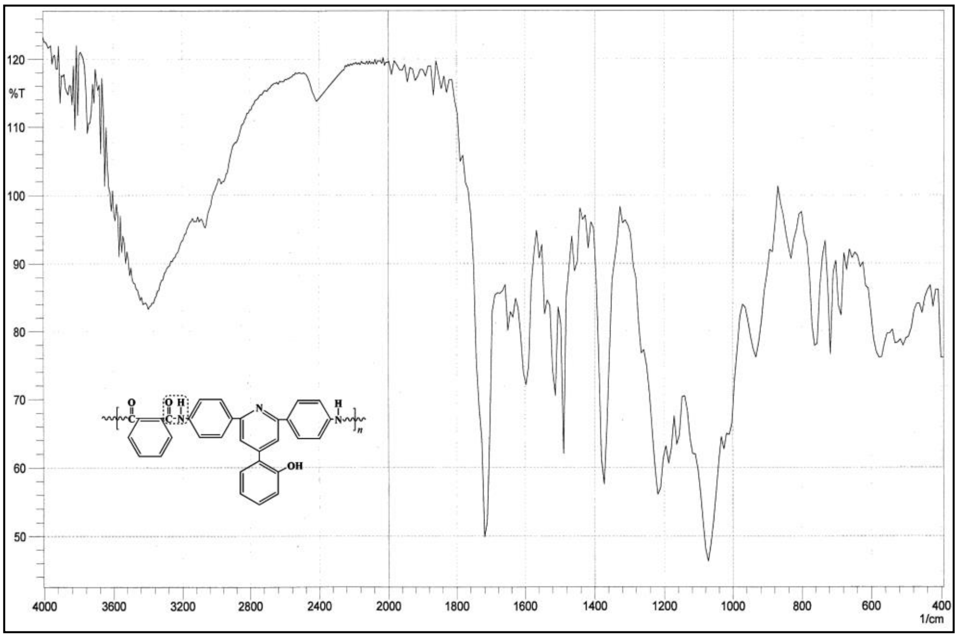


Figure 16 : FTIR spectrum of P_{ar}^2.

The *FTIR* spectrum of (P_{ar}^{3}) showed (**Figure 17**) absorption bands at ($3363cm^{-1}$) to (–NH stretching), ($3120cm^{-1}$) to (aromatic –CH stretching), the sharp bands at $(1735–1681)cm^{-1}$ to (C=O amide), $(1666–1573)cm^{-1}$ to (C=C) ring, $(1558–1519)cm^{-1}$ to (C=N), and ($632cm^{-1}$) to (C–Cl).

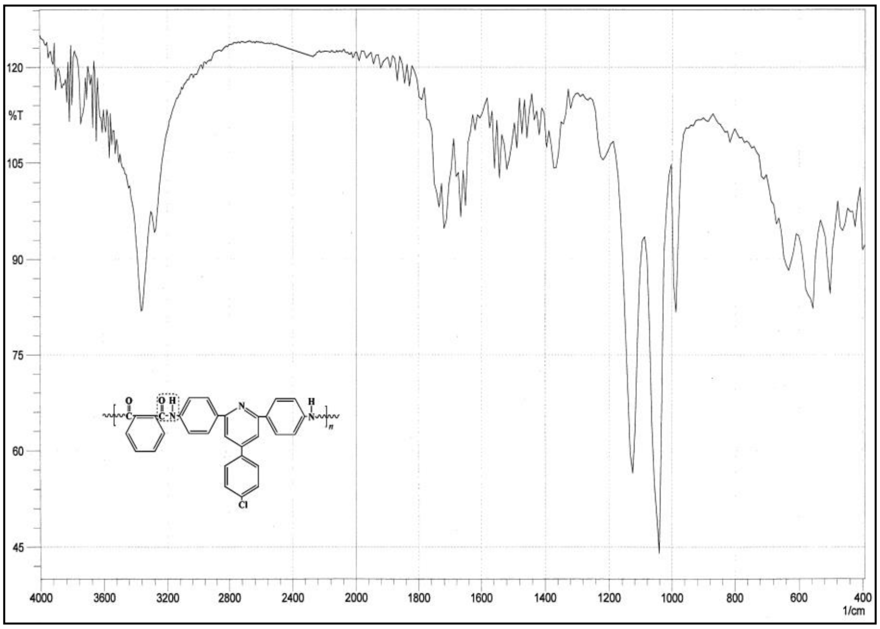


Figure 17 : FTIR spectrum of P_{ar}^{3}.

The *FTIR* spectrum of (P_{ar}^{4}) showed (**Figure 18**) absorption bands at (3365cm-1) to (–NH stretching), (3110cm-1) to (aromatic –CH stretching), the sharp bands at (1743–1674)cm-1 to (C=O amide), (1658–1550)cm-1 to (C=C) ring, and (1566–1512)cm-1 to (C=N).

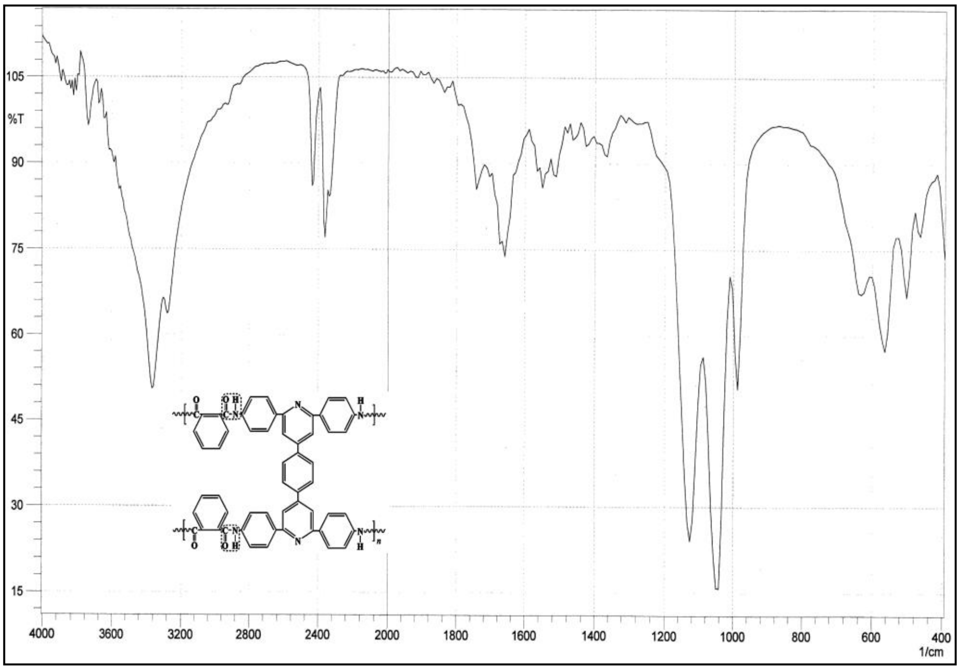


Figure 18 : FTIR spectrum of P_{ar}^{4}.

^{1}H-NMR spectra of P_{ar}^1, P_{ar}^3, and P_{ar}^4 :-

^{1}H-NMR spectrum of P_{ar}^1 in (**Figure 19**) shows a singlet at (2.249 δ ppm) to (6H, CH_3), a multiplet at (7.684-8.026 δ ppm) to (20H, Phenyl and hetero rings), and signal at (10.748 δ ppm) to (amide linkage).

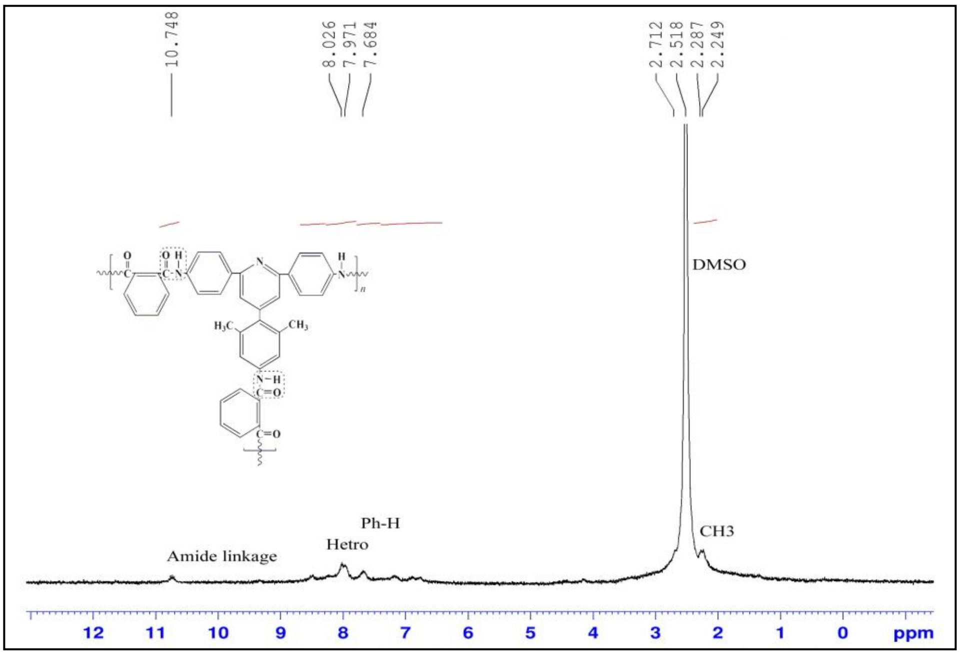


Figure 19 : ^{1}H-NMR spectrum of P_{ar}^1.

^{1}H-NMR spectrum of P_{ar}^3 in (**Figure 20**) shows a multiplet at (7.177-8.340 δ ppm) to (18H, Phenyl and hetero rings), and signal at (10.712 δ ppm) to (amide linkage).

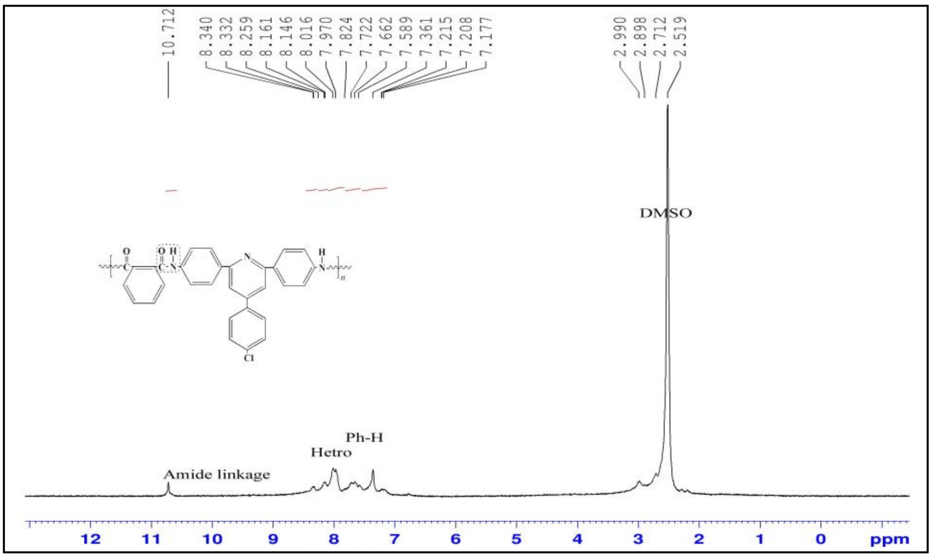


Figure 20 : ^{1}H-NMR spectrum of P_{ar}^3.

^{1}H-NMR spectrum of P_{ar}^4 in (**Figure 21**) shows a multiplet at (6.643-8.956 δ ppm) to (32H, Phenyl and hetero rings), and signal at (10.737 δ ppm) to (amide linkage).

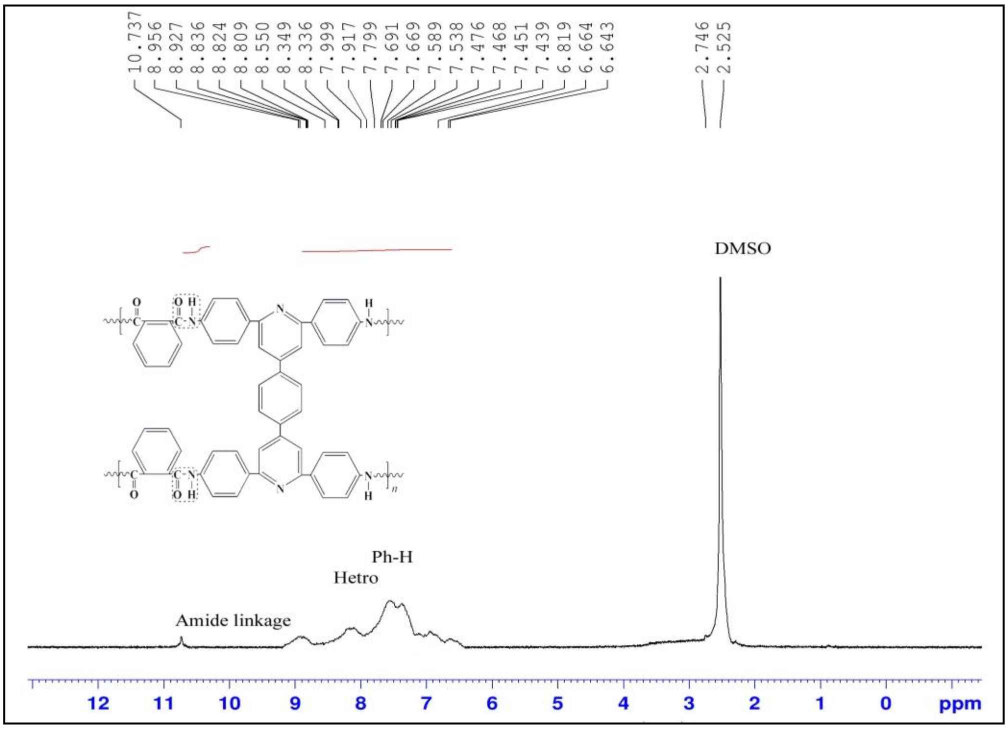
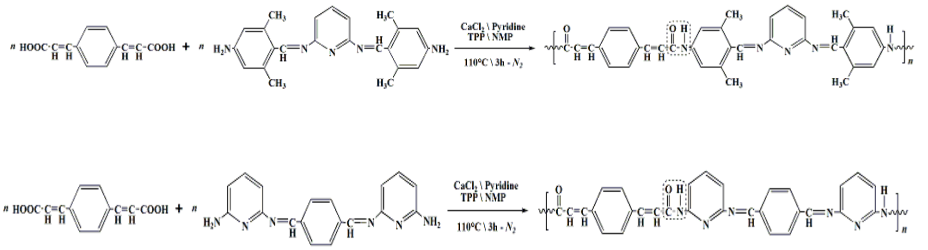


Figure 21 : ^{1}H-NMR spectrum of P_{ar}^4.

3.2.2 Synthesis of [P_{ar}^5 , P_{ar}^6] :-

In this section, we used Yamazaki method for synthesis of a series of **two** new polyamides from the direct polycondensation reaction of ***P*-phenylenediacrylic acid** with **two** new different aromatic diamines [**BADMDP** ***Schiff-Base***, and **BAPIDB** ***Schiff-Base***], respectively by using Lithium Chloride (LiCl); TPP and pyridine as condensing agents in NMP as solvent. These polymers have a soft segment such as vinyl moiety and Schiff-Base groups in main chain for improving solubility in organic solvents in compared to aromatic polyamides.

On the other hand, there is a considerable attention for synthesis polymers containing *P*-phenylenediacryloyl moiety in main chain, because they can used for preparing photosensitive liquid crystalline polymers. These polyamides were characterized by *FTIR* and ^{1}*H-NMR spectra*.



Scheme 13 : Synthesis of P_{ar}^{5} , P_{ar}^{6} respectively.

Characterization of [P_{ar}^{5} , P_{ar}^{6}] :-

The *FTIR* spectrum of (P_{ar}^{5}) showed (**Figure 22**) absorption bands at (3351cm^{-1}) to (–NH stretching), (3083cm^{-1}) to (aromatic –CH stretching), (2930cm^{-1}) to (aliphatic –CH stretching), the sharp band at (1666cm^{-1}) to (C=O amide), (1598cm^{-1}) to vinyl segment, (1570–1558)cm^{-1} to (C=C) ring, and (1502–1481)cm^{-1} to (C=N).

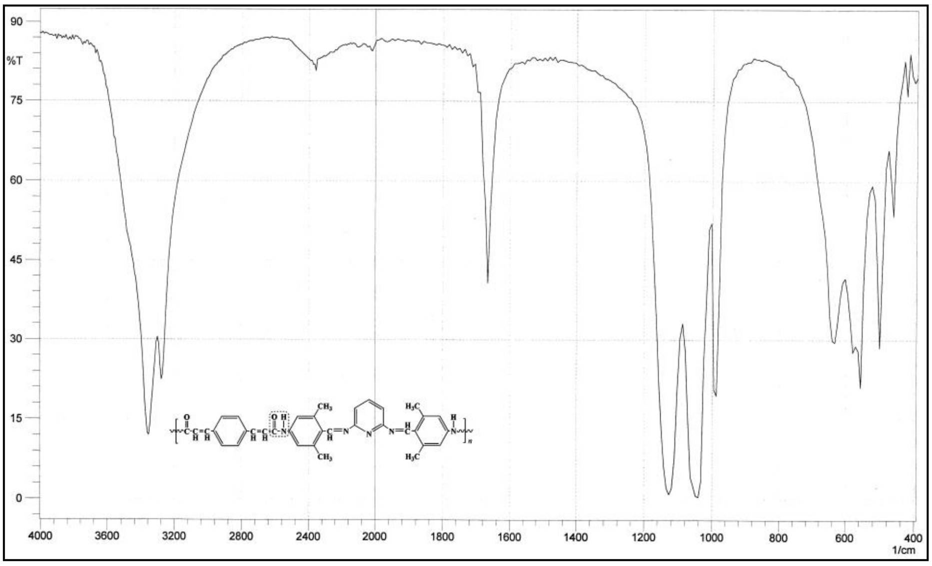


Figure 22 : FTIR spectrum of P_{ar}^{5}.

The *FTIR* spectrum of (P_{ar}^{6}) showed (**Figure 23**) absorption bands at (3352cm^{-1}) to (–NH stretching), (3080cm^{-1}) to (aromatic –CH stretching), (2926cm^{-1}) to (aliphatic –CH stretching), the sharp band at (1662cm^{-1}) to (C=O amide), (1594cm^{-1}) to vinyl segment, (1598–1560)cm^{-1} to (C=C) ring, and (1501–1480)cm^{-1} to (C=N).

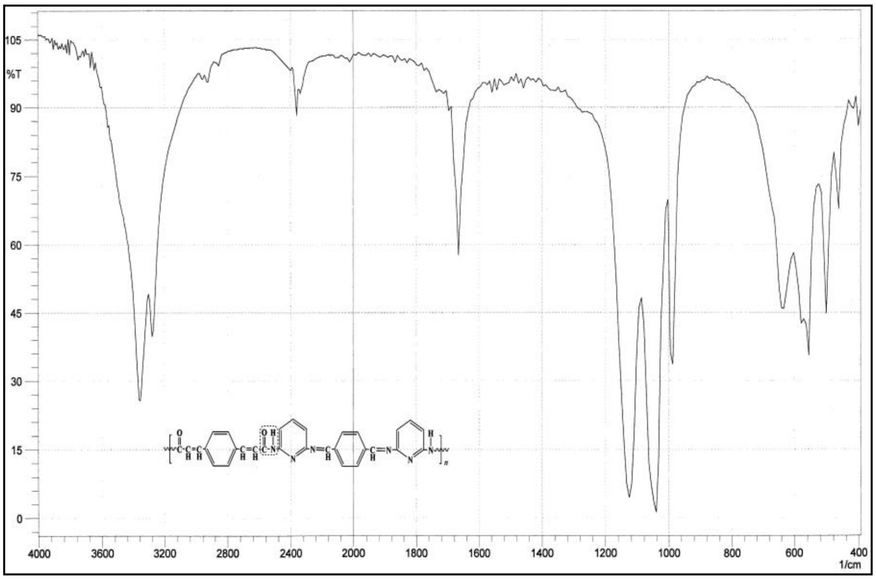


Figure 23 : FTIR spectrum of P_{ar}^{6}.

^{1}H NMR spectrum of P_{ar}^{5} in (**Figure 24**) shows a singlet at (2.269 δ ppm) to (12H, CH_3), a singlet at (5.662 δ ppm) to (2H, CH=CH), a multiplet at (7.215-8.259 δ ppm) to (11H, Phenyl and hetero rings), a singlet at (9.797 δ ppm) to (1H, CH=N), and signal at (10.609 δ ppm) to (amide linkage).

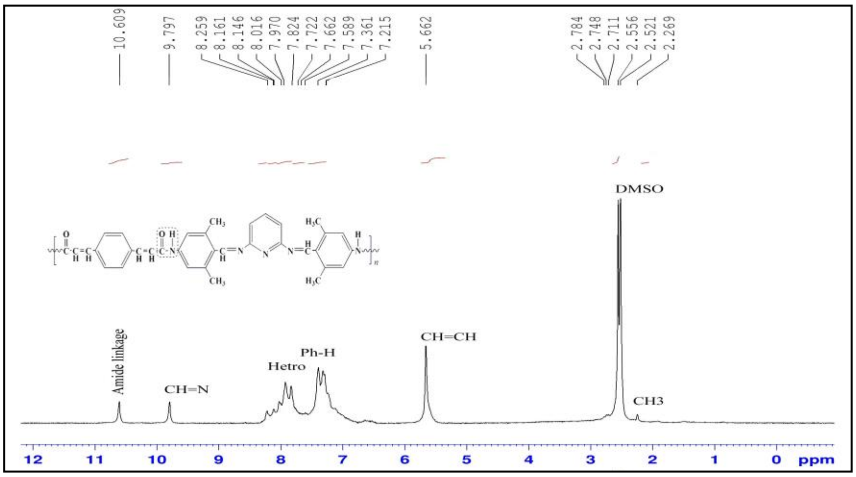


Figure 24 : ^{1}H-NMR spectrum of P_{ar}^{5}.

3.3 Solubility of polyamides :-

Solubility of polyamides [$\boldsymbol{P}$***ar***^{1}–$\boldsymbol{P}$***ar***^{6}] was qualitatively tested in organic solvents and the results are summarized in (Table 4). The method that attempt to enhance their processabilities and solubilities were either by introducing bulky groups, flexible linkages, or molecular asymmetry into the polymer backbones. In these manners, the attachment of bulky pendant groups in polymer backbone not only could provide an enhanced solubility because of decreased packing density and crystallinity, but also could impart an increase in Tg by restricting the segmental mobility[33].

One of the major objectives of this work was producing modified polyamides with improved solubility. The Solubility was investigated as (0.01gm) of polymeric sample in (2ml) of a solvent. All of the newly synthesized polyamides were readily good soluble in common polar and dipolar aprotic solvents, and better solubility in m-Cresol without need for heating.

Table 4 : Solubility of Polyamides [Par^1–Par^6]

Solvent	Polyamides					
	Par1	Par2	Par3	Par4	Par5	Par6
DMAc	+-	++	++	++	+-	+-
DMF	+++	+-	++	+++	+-	+-
NMP	++	++	++	++	++	++
Pyridine	++	++	++	++	++	+++
m-Cresol	+++	+++	++	+++	+++	+++
THF	+++	+++	+++	+++	++	++
$CHCl_3$	++	++	++	++	++	++
CH_2Cl_2	++	++	++	++	++	++
DMSO	+-	++	++	+++	++	++
Conc. H_2SO_4	++	++	++	++	++	++

Full Soluble.	+++
Soluble at room.T.	++
Partially Soluble.	+ -

3.4 Thermal analysis of polyamides :-

The thermal properties of six samples of these polyamides were investigated by means of thermogravimetric analysis (**TGA**) and derivative thermogravimetric (**DTG**) analysis in a nitrogen atmosphere at a heating rate of 10°C/min and the results such as T_i , T_{op} , T_f , $T_{50\%}$, T_s , and char yields at 700°C are summarized in (**Table 5**). The temperatures of 50% weight loss of polymers as a standard indication for thermal stability of polymers were all above 700°C, which indicates excellent thermal stability of polymers. The stability of the polymer increased with the increased content of aromatic rings. The char yields of these polymers at 700°C were 65% and 91% in nitrogen, which was good for polyamides. All the polymers left more than 65% char yields at 700°C in nitrogen, which indicate they could meet high temperature resistant requirements as some special materials in modern aerospace, military and microelectronics industries. However, the weight residue of $\mathbf{P_{ar}^4}$ and $\mathbf{P_{ar}^6}$ at 700°C were the highest for any polyamide of this series, (83.6% and 91%) respectively.

Polyamides containing phenyl group as substituent in the pyridine ring had maximum thermal stability. It seems that using a bulkier substituent in the *4-position* of the pyridine ring of diamine monomers causes improvement of solubility and thermal stability of resulting polyamides.

Table 5 : Thermal behavior data of Polyamides

Polyamides	DT/°C				$T_{50\%}$	T_s	Char% *at 700°C*
	T_i	T_{op1}	T_{op2}	T_f			
P_{ar}^1	225	260	580	620	>700	572	68.5
P_{ar}^2	250	316	535	>700	>700	556	67.5
P_{ar}^3	225	256	503	555	>700	>700	76.5
P_{ar}^4	255	300	500	>700	>700	>700	83.6
P_{ar}^5	220	260	---	315	>700	>700	82.3
P_{ar}^6	160	230	---	250	>700	>700	91.0

DT : Decomposition temperature.
T_i : Initial decomposition temperature.
T_{op} : Optimum decomposition temperature.
T_f : Final decomposition temperature.
$T_{50\%}$: Temperature of 50% weight loss, obtained from TGA.
T_s : Softening temperature.
Char% at 700°C : Residual weight percentage at 700°C in nitrogen by TGA.

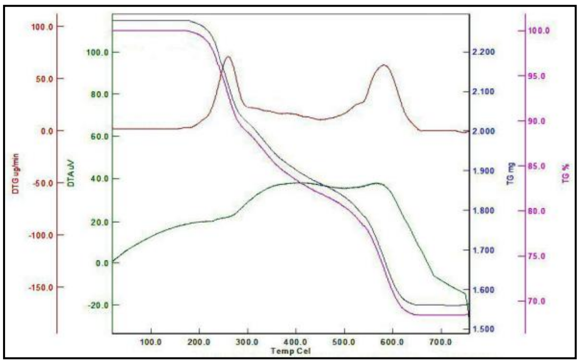


Figure 25 : TGA curve of P_{ar}^1.

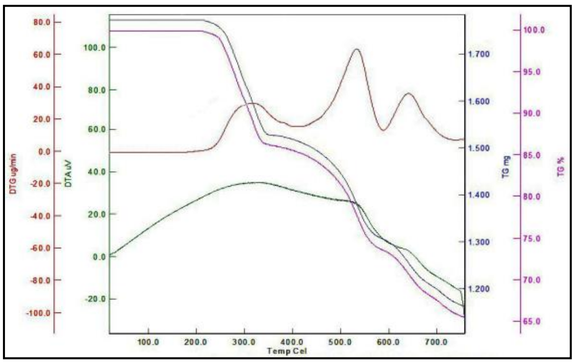


Figure 26 : TGA curve of P_{ar}^2.

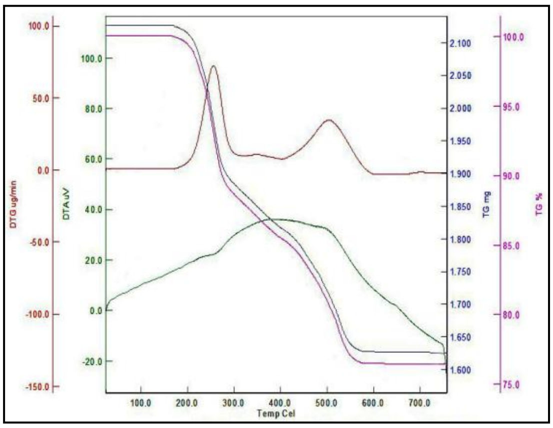


Figure 27 : TGA curve of P_{ar}^3.

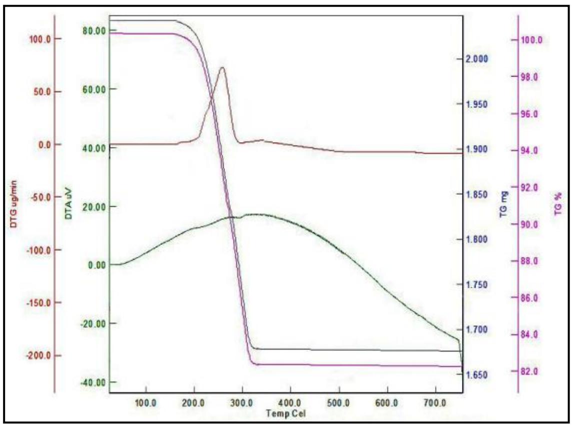


Figure 29 : TGA curve of P_{ar}^5.

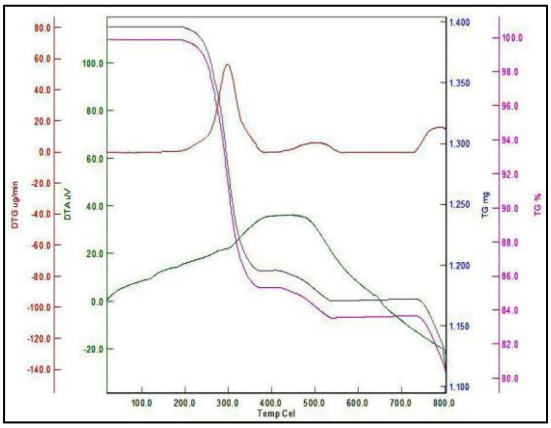


Figure 28 : TGA curve of P_{ar}^4.

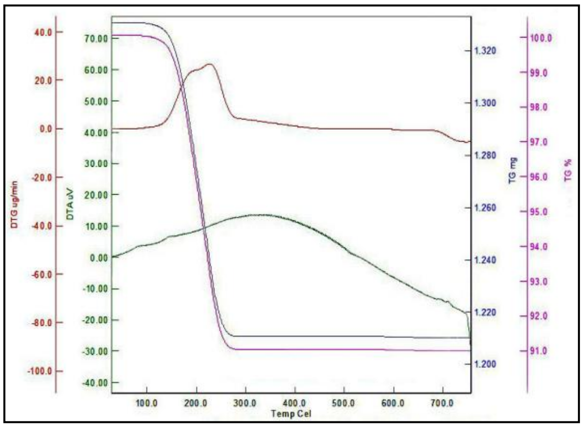


Figure 30 : TGA curve of P_{ar}^6.

4. Conclusion

A series of new aromatic polyamides were synthesized from new synthesized aromatic *di*, *tri*, and *tetra* amines : (ADPBAP, HPBAP, CPBAP, BAPPBAP, BADMDP, and BAPIDB) with various aromatic diacids (Phthalic acid, and *p*-Phenylenediacrylic acid) via the direct amidation Yamazaki's method in the presence of $CaCl_2$ or LiCl in Pyridine and TPP as condensing agents in NMP as solvent, and characterized by *IR*, and ^{1}*H-NMR* techniques.

Solubility of polyamides was tested in different solvents, such as DMAc, DMF, NMP, Pyridine, m-Cresol, THF, $CHCl_3$, CH_2Cl_2, DMSO, and *Conc*.H_2SO_4, and showed very good solubility without need for heating.

Thermal stability of polyamides was evaluated by dynamic thermogravimetric analysis (**TGA**) and derivative thermo- gravimetric (**DTG**) analysis in a nitrogen atmosphere at a heating rate of 10°C/min at 700°C and showed excellent thermal stability.

The temperatures of 50% weight loss were all above 700°C, and the char yields at 700°C were 65% and 91% in nitrogen, the weight residue of $\mathbf{P}_{ar}^{4}$ and $\mathbf{P}_{ar}^{6}$ at 700°C were the highest from any polyamide of this series, (83.6% and 91%) respectively. These new Polyamides containing pyridine heterocyclic ring, and Schiff-Base linkages showed better solubility and excellent thermal stability.

These specifications may qualifies these Polyamides for use in different applications such as gas separation membranes, engineering plastics, polymer blends, composites, some special materials in modern aerospace and military, microelectronics industries, and thermal insulation.

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*تخليق وتشخيص بولي أميدات أروماتية محتوية على حلقة بيريدين غير متجانسة وروابط شف-بيس.

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الخلاصة:

ستة من البولي أميدات الاروماتية الجديدة $\mathbf{P_{ar}^{1}}$ - $\mathbf{P_{ar}^{6}}$ حضرت بوساطة تفاعل بلمرة التكثيف المباشرة (طريقة يامازاكي) : حامض بارا-فنيلين ثنائي الاكريلك (4-Phenylenediacrylic acid) مع اثنين من مونيمرات ثنائية الأمين الجديدة الحاوية على روابط شف-بيس وهي (BADMDP, BAPIDB) ; وحامض الفثالك (PA) مع أربع مونيمرات جديدة ثنائية الأمين حاوية على حلقة بيريدين غير متجانسة ، وهذه الحلقة تحمل مجاميع أروماتية كبيرة متدلية في الموقع (**4**) من حلقة البيريدين وهي (ADPBAP, HPBAP, CPBAP, BAPPBAP) بوجود كلوريد الكالسيوم في البيريدين وثلاثي فينيل فوسفيت كعوامل تكثيف في مركب N-مثيل-2- بايروليدينون كمذيب. حامض بارا-فنيلين ثنائي الاكريلك (PPDAA) حضر عن طريق تفاعل تكثيف التيريفثال الديهايد مع حامض المالونيك بوجود البيريدين. هذه المونيمرات المحضرة شخصت بواسطة تقنيتي طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي. البولي أميدات الناتجة شخصت بوساطة تقنيتي طيف الأشعة تحت الحمراء وطيف الرنين النووي المغناطيسي، فضلا عن دراسة خواصها الفيزيائية بما في ذلك الذوبان ، والاستقرار الحراري والسلوك الحراري. كل هذه البولي أميدات الاروماتية الجديدة أظهرت قابلية ذوبان جيدة جدا في المذيبات العضوية الشائعة واستقرارية حرارية ممتازة.

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