

# New Flame-retardant and Thermally Stable Polyimides Based on Pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetra- carboxylic dianhydride (BTDA with diamines containing halogens and phosphorus components in the Main Chain: Synthesis and Characterization

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**Abstract**---Five new flame retardant aromatic polyimides containing phosphine oxide, ether and Schiff base moieties in the main chain were synthesized by the solution polycondensation reaction of dianhydrides, Pyromellitic dianhydride (PMDA) and 3,3',4,4'-benzophenone tetra carboxylic dianhydride (BTDA) with various structurally different diamines containing halogens and phosphorus components using a standard two-stage process with thermal imidization of poly(amic acid). The polymerization reactions produced a series of flame retardant with high yields. The resulting polymers were fully characterized by means of FTIR and <sup>1</sup>H-NMR spectroscopy, elemental analyses and solubility tests. The thermal properties and flame retardant behaviour of the aromatic polyimides investigated using thermal gravimetric analyses. Data obtained by the thermal analyses revealed that the polymers showed good thermal stability and also high char yields, in the TGA data indicating that aromatic polyimides (P1-P5) have good flame retardant properties and thermal stability.

Furthermore, high char yields in TGA analysis values indicate that the aromatic polyimides containing halogens and phosphorus components exhibit excellent flame retardant properties. All of these new polymers show good solubility in polar aprotic solvents.

**Keywords**---Aromatic polyimides, Pyromellitic dianhydride (PMDA), 3,3',4,4'-benzophenone tetra- carboxylic dianhydride (BTDA), Flame Retardant

## I. INTRODUCTION

During the previous decades, conventional materials such as metals, wood, glass and ceramics were increasingly replaced by synthetic polymers, due to their versatility, low density, good mechanical and physical properties and easy molding process[1,2]. However, these advantages of polymeric materials were shadowed by their easy flammability and low stability in high temperatures in comparison with metals. Aromatic polyimides are recognized as high-performance polymer materials, for their excellent mechanical strength and high thermal stability, as well as balanced mechanical and electric properties [3, 4]. However, most polyimides are difficult to process, due to their rigidity and poor solubility in organic solvents. Over the last few years, considerable attention has been paid to the preparation of flame-retardant polymers[5,6] and, among these,

phosphorus containing polymers are the most widely used[7-11]. Polymers containing phosphorus are generally flame retardant. They are also characterized by good adhesion to substrates, metal ion binding properties and increased polarity [12, 13]. Major advantages have polymers with phosphine oxide moieties. Phosphine oxide groups possess hydrolytically stable P-C and P-O-C bonds and oxidatively stable P=O bonds. Polymers containing phosphine oxide moieties typically display good flame resistance, high thermal oxidative stability, enhanced solubility and improved miscibility and adhesion [14-16]. Several methods have been developed for the preparation of polyimides, few of them are,[17]: A) Polyimides by polycondensation of diamine and dianhydride. B) Polyimides from dihalides and aromatic diimide. C) Polyimides from diisocyanates. Polymerization of Aromatic diamines and dianhydride can be carried out in two different ways :i) Preparation of poly (amic acid):- When Aromatic diamine and dianhydride are reacted into a dipolar aprotic solvent such as DMAc, NMP and DMF. ii) Imide Formation:- The poly(amic-acid) is heating later to dehydrate and the polyimide formation[18,19] . In order to improve solubility and processibility with maintaining thermal stability, it has been performed that some studies of introducing soft segments to the main chain of the polymers for example flexible ether and methylene groups into the polymer backbone ,Presence of carbonyl groups in BTDA-derived polyimides increased solubility in comparison with rigid PMDA-derived polyimide[20]. A most feasible approach for improving the flame retardant properties have been developed by incorporating additive- or reactive-type flame retardants into Aromatic polyimides[21] halogen and Phosphorus-containing compounds for flame retardants are used either by blending with polymers or by reacting onto polymers. It is believed that halogen and phosphorus containing compounds can quench flammable particles like H . or OH . and reduce the energy of the flame in the gas phase [22,23]. Moreover, in the solid phase ,the phosphorus-containing functional groups are converted by thermal decomposition to phosphoric acid [24]. The polyphosphoric acid esterifies, and dehydrates the

polymer, and then forms a protective carbonaceous layer. This protective layer is heat-resistant at higher temperatures, and shields the underlying polymer from attack by oxygen and radiant heat[25]. In the paper, syntheses of a series of new flame retardant aromatic polyimides containing halogen and Phosphorus components were synthesized by the reactions of direct polycondensation. The solubility, thermal stability were systematically investigated. These properties can make this polymer attractive for practical applications such as processable high-performance engineering plastic.

## II. EXPERIMENTAL

### 2.1 Materials

M-Cresol, Tetrahydrofuran (THF), Phosphoryl Chloride ( $\text{POCl}_3$ ), 2-Bromo aniline, Dimethyl Sulphoxide (DMSO), all from (SIGMA-ALDRICH/ Germany); Iron powder, 3-Bromo aniline, 4,4-diamino phenyl methane, 2,4-dichloro benzaldehyde, Thioglycolic acid, pyromellitic dianhydride (PMDA), all from (MERCK/ Germany); di Chloro phenyl phosphine oxide, Absolute Methanol, Ethyl methyl ketone, N-methyl-2-pyrrolidinone (NMP), all from (BDH/ England); Dichloromethane Hydrochloric acid, Absolute ethanol, N,N-dimethylformamide (DMF), p-nitro phenol, Triethylamine, Isoquinoline, 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA), all from (LTD / Tokyo).

### 2.2 Apparatus

FTIR 8400S, Fourier Transform infrared spectrophotometer, SHIMADZU, Japan), (Oven, Trip International Corp. Italy), (Measuring the degree of fusion (Melting Points) Stuart smp30 melting point apparatus), (Hot plate stir, Bibby Strlind, UK), ( $^1\text{H}$ NMR spectra were registered using a Bruker, Ultra, Shiel 300MHZ, Switzerland, at University's Educational teacher -Tehran Iran) using (DMSO- $d_6$ ) as solvent, and to the (Thermo Gravimetry analysis (TGA) were performed on a Polymer laboratories Co England, Model PL-TG at Iran polymer & petrochemical institute, using a heating rate of  $10^\circ\text{C}/\text{min}$  in Argon atmosphere within the temperature range of ( $25\text{--}800^\circ\text{C}$ ).

### 2.3 Synthesis of monomers :-

#### 2.3.1 Synthesis of 4-((4-amino-3-bromophenyl)(2,4-dichlorophenyl)methyl)-2-bromobenzamine (ABDB)

A mixture of 2-Bromo aniline (61.2 gm, 0.354 mol), 2,4-dichloro benzaldehyde (30.9 gm, 0.177 mol), HCl catalyst (10 ml- 0.35M) and Thioglycolic acid (0.5 gm -6mmol) promoter were placed in a three necked-round bottom flask equipped with a condenser, mechanical stirrer and thermometer and it was kept in a thermostat bath at  $60^\circ\text{C}$  for 6hs. Then, the reaction mixture was transferred to cold water to quench the reaction. Then, the product was filtered, dried under vacuum. Then product was dried and the yield was (78%) of dark brown crystals, M.p = ( $197\text{--}200^\circ\text{C}$ ), Figure 2-1 Structure of monomer (ABDB).

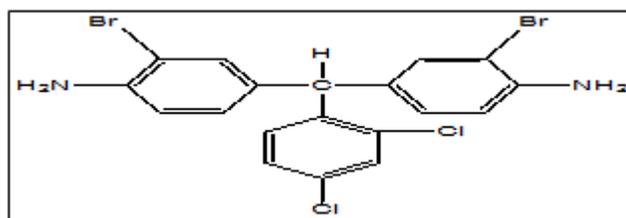


Fig 2.1 structure of monomers (ABDB)

#### 2.3.2 Synthesis of 2,2-Bis(p-hydroxyphenyl)-1,1,1-Trichloroethane (BHTE)

To a 1 L round bottom flask, equipped with a mechanical stirrer, thermometer, addition funnel, and purged with nitrogen, was added phenol (131 g, 1.3 mol), chloral hydrate (104 g, 0.63 mol) and acetic acid (120 mL). The reaction was sealed under nitrogen with a septum and placed in a cooling bath at  $0^\circ\text{C}$ . Concentrated sulfuric acid (60 mL) and acetic acid (60 mL) was added drop-wise via the addition funnel, over 90 min period. Then an additional 150 mL of sulfuric acid was added to the reaction mixture drop wise at a rate so that the internal temperature of the reaction never rose above  $5^\circ\text{C}$ . The mixture was then allowed to warm to room temperature overnight (12 h). The reaction mixture was then quenched with ice and water and diluted to twice its volume. The precipitated powder was then filtered through a fritted filter and washed with copious amounts of water (3 L) to remove all excess acid. The resulting solid was then dried for 24 h in a vacuum oven at  $95^\circ\text{C}$ . M.P  $204\text{--}206^\circ\text{C}$ . Figure 2-2 Structure of Derivative (BHTE).

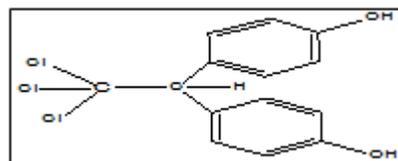


Fig 2.2 structure of Derivative (BHTE)

#### 2.3.3 Synthesis of 2,2-bis(4-(4-nitrophenoxy)phenyl)-1,1,1-trichloroethane (BNPT)

A mixture of [BHTE] (3.06 gm, 10 mmol), p-chloronitrobenzene (4.74 gm, 32 mmol), potassium carbonate (7 gm, 50 mmol), and (20 ml) of DMF was refluxed at  $140\text{--}142^\circ\text{C}$  for 8hs under nitrogen atmosphere. After completion of the reaction, the reaction mixture was added to water to precipitate product [28]. The resulting solid was filtered and recrystallized from (2-methoxyethanol) to produce 5.36 gm (80% wt) of deep brown crystals. m.p  $255\text{--}258^\circ\text{C}$ . Figure 2-3 Structure of Derivative (BNPT).

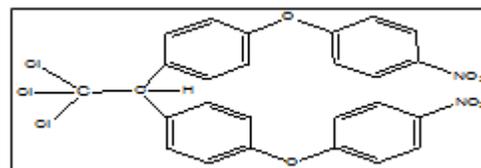


Fig 2.3 structure of Derivative (BNPT)

#### 2.3.4 Synthesis of 2,2-bis(4-(4-aminophenoxy)phenyl)-1,1,1-trichloroethane (BAPT)

A (500ML), 3-neck, round-bottom flask fitted with a mechanical stirrer, an addition funnel, and a condenser, Iron

powder (8 gm) was added portion wise with stirring to a hot mixture of (**BNPT**) (4.96 gm, 0.02 moles) in ethyl alcohol (20 ml) and concentrated hydrochloric acid (30 ml) at reflux temperature. After completion of the addition, the refluxing was continued for 6 hours at 78 °C. Upon cooling a Dark brown precipitate formed, which was filtered off, washed with water, dried and recrystallized. Yields: 65%, Melting point: 295-298 °C. Figure ( 2-4) Structure of monomer (**BNPT**).

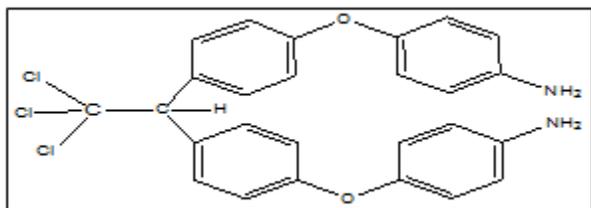


Fig 2.4 structure of monomers (**BNPT**)

### 2.3.5 Synthesis of Bis(4-nitro phenyl)chloro phosphonate (**MP1**).

A 1-liter (L), 3-neck, round-bottom flask fitted with a mechanical stirrer, an addition funnel, and a condenser with a nitrogen inlet, a thermometer was charged with 4-nitrophenol (102.9 g, 0.74 mol), Triethylamine (103 mL, 75 g, 0.74 mol), and Tetrahydrofuran (THF, 250 mL). The solution was cooled with an ice water bath. A solution of Phosphoryl Chloride (POCl<sub>3</sub>) (56.8 g, 0.37 mol) in 200 mL of THF was added drop wise over a period of 30 minutes. The reaction mixture was stirred overnight and allowed to warm to room temperature. The reaction mixture was poured into 1 L of stirred water and the resulting precipitate was collected by vacuum filtration[19]. The solid was dried in a vacuum oven at 55°C for 4 hours to give 110.86 g (85%) of White crystalline solid, m.p of 118°-121° . Figure 2-5 Structure of Derivative (**MP1**)

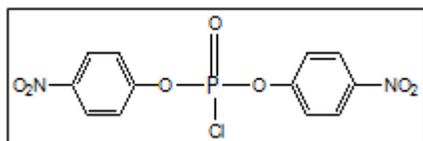


Fig 2.5 Structure of Derivative (**MP1**)

### 2-3-6 Synthesis of Bis (4-amino phenyl) chloro phosphonate (**BACP**)

A (500ML), 3-neck, round-bottom flask fitted with a mechanical stirrer, an addition funnel, and a condenser , Iron powder (8 gm) was added portion wise with stirring to a hot mixture of (**MP1**) (5.96 gm, 0.02 moles) in ethyl alcohol (20 ml) and concentrated hydrochloric acid (30 ml) at reflux temperature. After completion of the addition, the refluxing was continued for 6 hours at 78 °C. Upon cooling a Dark brown precipitate formed, which was filtered off, washed with water, dried and recrystallized . Yields: 60%, Melting point: 310-312 °C. Figure( 2-6) Structure of monomer (**BACP**).

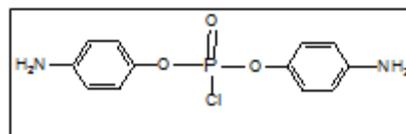


Fig 2.6 Structure of monomer (**BACP**).

### 2.3.7 Synthesis of 4-((4-amino-3-bromophenyl)(4-bromophenyl)methyl)-2-bromobenzenamine (**ABBB**).

A mixture of 2-bromo aniline (61.2 gm , 0.354mol), 4-bromo benzaldehyde ( 25.9 gm , 0.177 mol ), HCl catalyst (10 ml- 0.35M) and Thioglycolic acid (0.5gm -6mmol) promoter were placed in a three necked-round bottom flask equipped with a condenser, mechanical stirrer and thermometer and it was kept in a thermostat bath at 60°C for 6hs. Then, the reaction mixture was transferred to cold water to quench the reaction. Then, the product was filtered, dried under vacuum .Then product was dried and the yield was (82%) of dark black crystals , M.p = (222-225°C), Figure 2-7 Structure of monomer (**ABBB**).

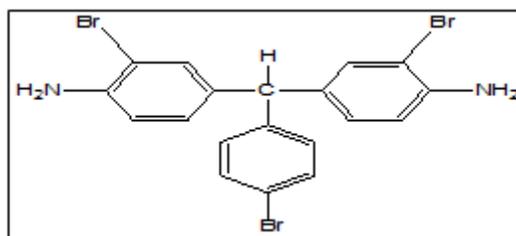


Fig 2.7 structure of monomers (**ABBB**)

### 2.3.8 Synthesis of N-(4-((4-((4-amino-3-bromophenyl)(4-bromophenyl)methyl)-2(bromophenylimino)methyl benzylidene)-4-((4-amino-3-bromophenyl)(4-bromophenyl)methyl)-2-bromobenzenamine (Schiff-base)(**SB1**)

This monomer was prepared by the condensation of monomer (**ABBB**) (3gm , 20mmol) and Terephthalaldehyde (1.1gm, 10mmol) in 15ml of methanol, by boiling the mixture under reflux for 3hs. The precipitated was filtered and recrystallized from methanol and dried in a vacuum desiccators and gave 2.93gm (79%wt) of light green crystals. m.p 287-289°C. Figure 2-8 Structure of monomer(**SB1**).

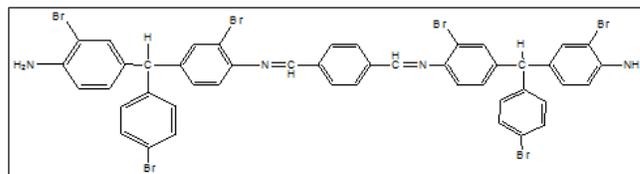


Fig 2.8 structure of monomers (**SB1**)

### 2.3.9 Synthesis of N-(4-((4-((4-amino-3-bromophenyl)(2,4-dichlorophenyl)methyl)-2-bromophenylimino)methyl)benzylidene)-4-((4-amino-3-bromophenyl)(2,4-dichlorophenyl)methyl)-2-bromobenzenamine (Schiff-base)(**SB2**)

This monomer was prepared by the condensation of monomer (**ABDB**) (4.6gm , 20mmol) and Terephthalaldehyde (1.1gm, 10mmol) in 15ml of methanol, by boiling the mixture under reflux for 3hs. The precipitated was filtered and recrystallized from methanol and

dried in a vacuum desiccators and gave 3.43gm (81%wt) of deep yellow crystals. m.p 322-325°C. Figure 2-9 Structure of monomer (SB2).

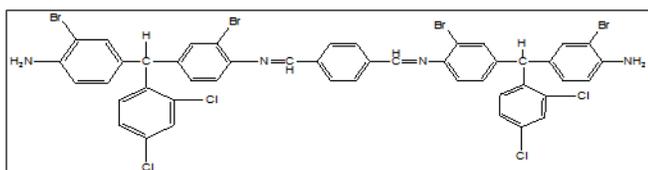


Fig 2.9 structure of monomers (SB2)

### 2.4 Synthesis of polymers

A 500ml three neck round flask equipped with a nitrogen inlet, a thermometer, and a mechanical stirrer and a condenser. was charged with (1.4 mmol) Aromatic diamine to (10ml) m-Cresol containing a catalytic amount of (0.5 ml) isoquinoline for ,0.5 h at room temperature. A stoichiometric quantity of (1.4 mmol) dianhydride was added, the solids content was adjusted to 20% (w/w), the reaction was heated to 200 °C and stirred at 200 °C under a nitrogen atmosphere for (4-6 h) to form a viscous solution. The cooled polyimide solution was diluted with m-cresol and poured into ethanol in a blender to precipitate a fibrous solid that was isolated, subsequently washed in boiling methanol twice and dried in air at 150 C for 4 h [26]. **Table 2-1** : Synthesis of Aromatic polyimides . **Figure 2-10** : Repeating units of Aromatic polyimides.

TABLE 2.1  
SYNTHESIS OF AROMATIC POLYIMIDES.

Aromatic Polyimides	Monomers		Di anhydride gm/1.4mmol	Aromatic diamine gm/1.4mmol		Color
	Di anhydride	Aromatic diamine				
P1	PMDA	ABDB	0.305 g	0.700 g	83	brown
P2	BTDA	ANPT	0.451 g	0.696 g	87	light yellow
P3	BTDA	BACP	0.451 g	0.417 g	85	white
P4	PMDA	SB1	0.305 g	1.561g	80	dark brown
P5	PMDA	SB2	0.305 g	1.290g	77	brown

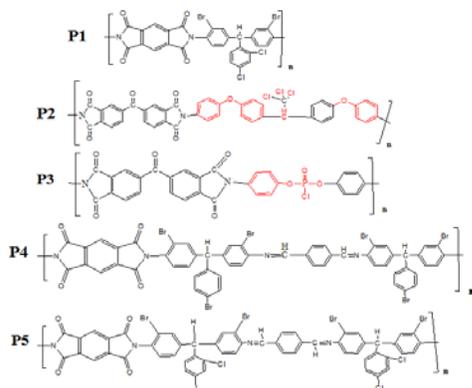


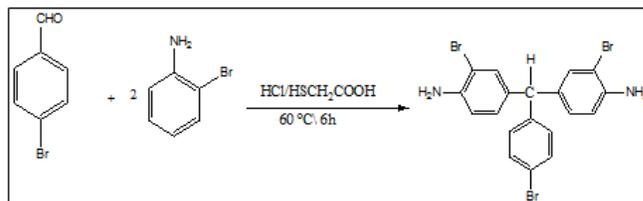
Fig 2.10 Repeating units of Aromatic polyimides

## III. RESULT AND DISCUSSION.

### 3.1 Synthesis and Characterization of monomers.

#### 3.1.1 Synthesis and Characterization of (ABBB).

The (ABBB) was synthesized from the reaction of two moles of ( 2-Bromo aniline) with one mole of (4-bromo benzaldehyde) and Thioglycolic acid promoter in presence of HCl as catalyst by condensation for 6 hrs. at 60 °C as shown in Scheme (3-1).



Scheme 3.1 Synthesis of (ABBB)

#### Characterization of (ABBB) IR-Spectra.

The FT-IR spectrum of (ABBB) (Figure 3-1) shows absorption bands at (3332,3209cm<sup>-1</sup>) to (NH<sub>2</sub>), (3031cm<sup>-1</sup>) to (aromatic C-H stretching), (2885,2823) cm<sup>-1</sup> to Aliphatic C-H , (1627, 1434)cm<sup>-1</sup> to (C=C) ring, (1311cm<sup>-1</sup>) to (C-N) and (1010cm<sup>-1</sup>) to (C-Br) .

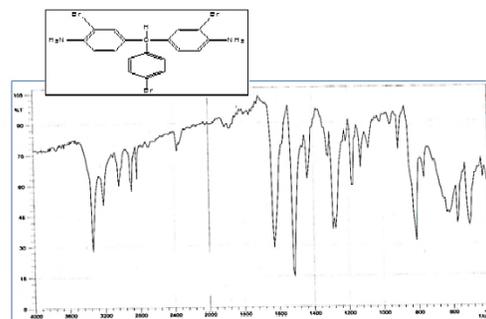
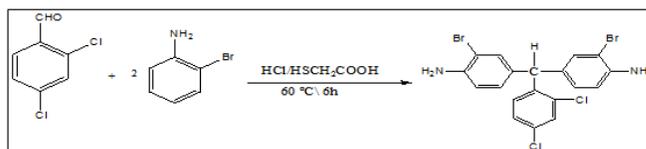


Fig 3.1 : FTIR spectrum of (ABBB)

#### 3.1.2 Synthesis and Characterization of (ABDB)

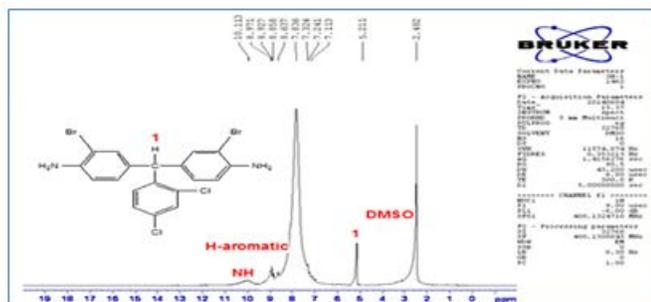
The (ABDB) was synthesized from the reaction of two moles of ( 2-Bromo aniline) with one mole of (2,4-di chloro benzaldehyde) and Thioglycolic acid promoter in presence of HCl as catalyst by condensation for 6 hrs. at 60 °C. as shown in Scheme (3-2)



Scheme 3-2 Synthesis of (ABDB)

#### <sup>1</sup>H NMR spectrum of (ABDB).

<sup>1</sup>H-NMR spectrum of ABDB in (Figure 3-2) shows a singlet at (5.21 δ PPM) to (1H , C<sub>1</sub>). a multiplet at (7.1-8.9δ ppm) to (9H, phenyl rings). and a singlet at (10.1δ ppm) to (4H, NH<sub>2</sub>)[20].

Fig 3.2:  $^1\text{H}$ -NMR spectrum of (ABDB)

#### Characterization of (ABDB) IR-Spectra.

The FT-IR spectrum of (ABDB) (Figure 3-3) shows absorption bands at ( $3394, 3247\text{cm}^{-1}$ ) to ( $\text{NH}_2$ ), ( $3085\text{cm}^{-1}$ ) to (aromatic C-H stretching), ( $2939, 2846$ )  $\text{cm}^{-1}$  to aliphatic C-H), ( $1589, 1488\text{cm}^{-1}$ ) to ( $\text{C}=\text{C}$  ring), ( $1342\text{cm}^{-1}$ ) to (C-N), ( $1010\text{cm}^{-1}$ ) to (C-Br) and ( $1046\text{cm}^{-1}$ ) to (C-Cl).

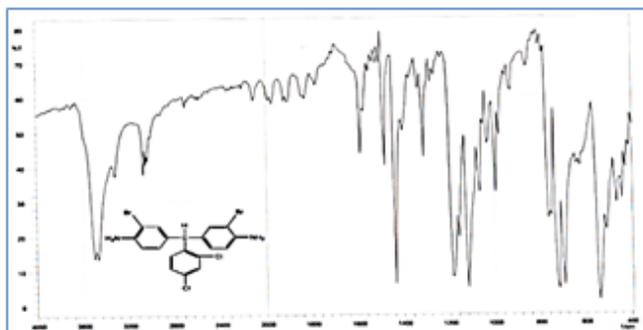
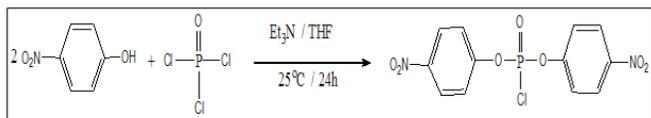


Fig3.3 : FTIR spectrum of (ABDB)

#### 3-1-3 Synthesis and Characterization of (MP1).

The (MP1) was synthesized from the reaction of (4-nitrophenol) with (Phosphoryl Chloride) and (Tetrahydrofuran) as solvent and (Triethylamine) as catalyst by stirred overnight and allowed to warm to room temperature, as shown in Scheme (3-3).



Scheme 3.3 Synthesis of (MP1)

#### Characterization of (MP1) IR-Spectra.

The FTIR spectrum of (MP1) (Figure 3-5) shows absorption bands at ( $3085\text{cm}^{-1}$ ) to (aromatic C-H stretching), ( $1612, 1488\text{cm}^{-1}$ ) to ( $\text{C}=\text{C}$  ring), ( $1350\text{cm}^{-1}$ ) to ( $\text{NO}_2$ ), ( $1311\text{cm}^{-1}$ ) to ( $\text{P}=\text{O}$ ), ( $1164\text{cm}^{-1}$ ) to ( $\text{P}-\text{O}$ ) and ( $547\text{cm}^{-1}$ ) to ( $\text{P}-\text{Cl}$ ).

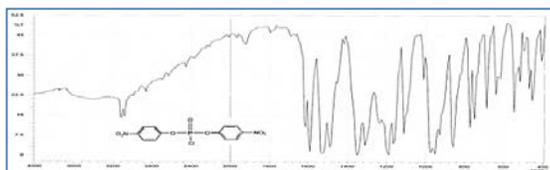
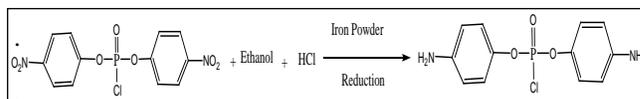


Fig3.4: FTIR spectrum of (MP1).

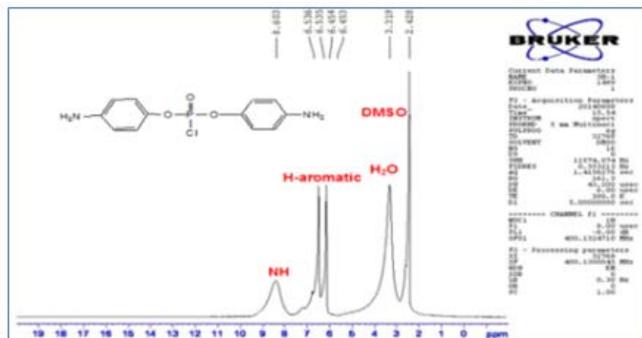
#### 3-1-4 Synthesis and Characterization of (BACP).

The catalytic hydrogenation of nitro group in the (MP1 to amino compound BACP) was accomplished by using ethyl alcohol and concentrated hydrochloric acid catalytic amount of Iron powder as reducing agent at  $78^\circ\text{C}$  for 6h, as shown in Scheme (3-4)



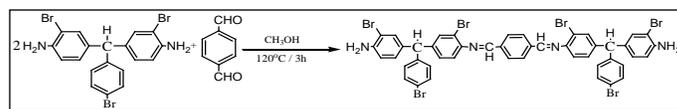
#### $^1\text{H}$ NMR spectrum of (BACP)

$^1\text{H}$ -NMR spectrum of (BACP) in (Figure 3-6) shows a singlet at ( $3.3\delta$  PPM) to ( $\text{H}_2\text{O}$ ), a multiplet at ( $6.4-6.5\delta$  ppm) to (8H, phenyl rings), and a singlet at ( $8.6\delta$  ppm) to (4H,  $\text{NH}_2$ ).

Fig 3.5 :  $^1\text{H}$ -NMR spectrum of (BACP)

#### 3.1.5 Synthesis and Characterization of (SB1)

(SB1) is prepared by the condensation of two moles of monomer (ABBB) with one mole of Terephthalaldehyde in the presence of methanol for 3hs, as shown in Scheme (3-5).



Scheme 3.5 Synthesis of (SB1)

#### Characterization of (SB1) IR-Spectra.

The FT-IR spectrum of ((SB1) (Figure 3-5) shows absorption bands at ( $3317\text{cm}^{-1}$ ) to ( $\text{NH}_2$ ), ( $3085\text{cm}^{-1}$ ) to (aromatic C-H stretching), ( $2970$ )  $\text{cm}^{-1}$  to aliphatic C-H), ( $1465, 1589\text{cm}^{-1}$ ) to ( $\text{C}=\text{C}$  ring), ( $1550-1535\text{cm}^{-1}$ ) to ( $\text{C}=\text{N}$ ), ( $1026\text{cm}^{-1}$ ) to (C-Br).

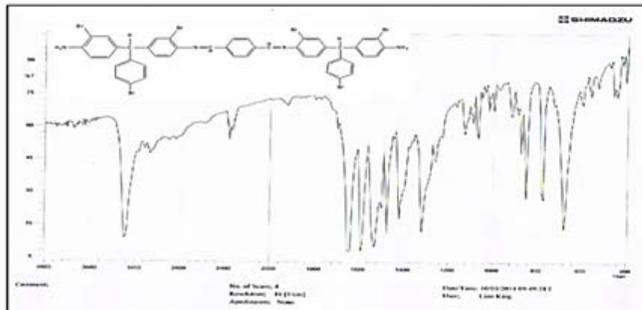
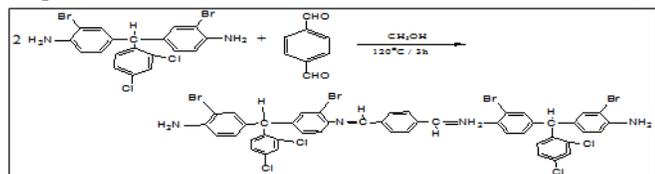


Fig 3.6: FTIR spectrum of (SB1).

### 3.1.6 Synthesis and Characterization of (SB2).

**SB2** is prepared by the condensation of two moles of monomer **ABDB** with one mole of **Terephthalaldehyde** in the presence of methanol for 3hs. as shown in Scheme (3-6).



Scheme 3-6 Synthesis of (SB2)

#### Characterization of (SB2) IR-Spectra.

The FT-IR spectrum of ((**SB1**)) (Figure 3-6) shows absorption bands at (3410 $\text{cm}^{-1}$ ) to ( $\text{NH}_2$ ), (3075 $\text{cm}^{-1}$ ) to (aromatic C-H stretching), (2970)  $\text{cm}^{-1}$  to aliphatic C-H), (1460,1580) $\text{cm}^{-1}$  to (C=C) ring, (1018-  $\text{cm}^{-1}$ ) to (C-Cl) , (1033 $\text{cm}^{-1}$ ) to (C-Br) .

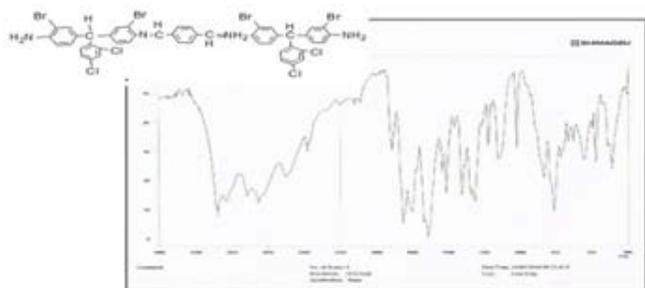
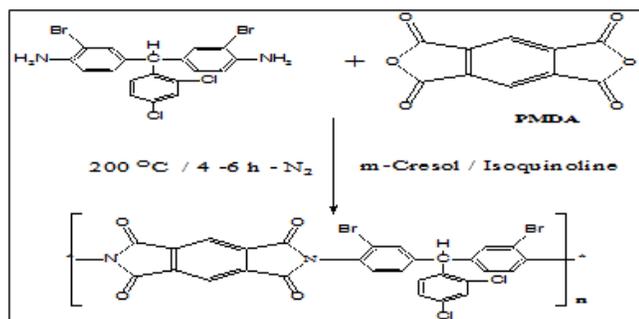


Fig 3.7 FTIR spectrum of (SB2).

### 3-2 Synthesis and Characterization of Aromatic Polyimides.

#### 3-2-1 Synthesis and Characterization of (P1).

Aromatic polyimide (**P1**) were prepared by polycondensation of equimolar an (**ABDB**) with (**PMDA**) at 200 °C for (4-6 hrs.). in the presence of( isoquinoline) as catalytic and( m-Cresol) as solvent under a dry nitrogen atmosphere , as in Scheme (3-7) Aromatic polyimide (**P1**)



Scheme 3.7 Synthesis of P1

#### $^1\text{H NMR}$ spectrum of (P1).

$^1\text{H-NMR}$  spectrum of **P1** in (Figure 3-8) shows a singlet at (5.54  $\delta$  ppm) to (1H,  $\text{C}_1$ ), amultiplet at (6.62-8.25  $\delta$  ppm) to (11H, phenyl rings).

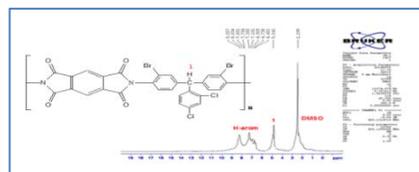


Fig 3.8  $^1\text{H-NMR}$  spectrum of (P1)

#### Characterization of (P1) IR-Spectra.

The FTIR spectrum of (**P1**) (Figure 3-9) shows absorption bands at (3078 $\text{cm}^{-1}$ ) to (aromatic C-H stretching), (2923,2854)  $\text{cm}^{-1}$  to Aliphatic C-H) , (1620, 1504)  $\text{cm}^{-1}$  to (C=C) ring, (1782,1720 $\text{cm}^{-1}$ ) to (C=O imide), (1388 $\text{cm}^{-1}$ ) to (C-N) and (1026  $\text{cm}^{-1}$ ) to (C-Br).

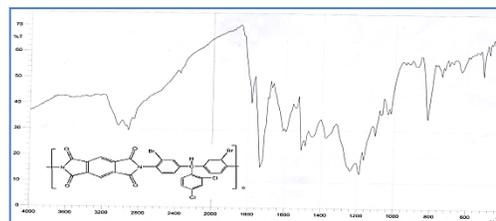
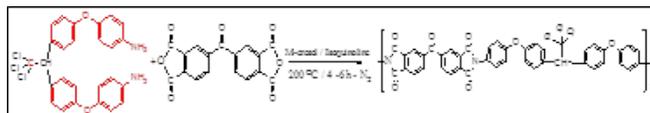


Fig 3.9 FTIR spectrum of (P1).

#### 3-2-2 Synthesis and Characterization of (P2).

Aromatic polyimide (**P2**) were prepared by polycondensation of equimolar an (**ANPT**) with (**BTDA**) at 200 °C for (4-6 hrs.). in the presence of( isoquinoline) as catalytic and( m-Cresol) as solvent under a dry nitrogen atmosphere , as in Scheme (3.8) Aromatic polyimide (**P2**).Scheme 3.8: Synthesis of P2



Scheme 3.8: Synthesis of P2

#### Characterization of (P2) IR-Spectra.

The FTIR spectrum of (**P2**) (Figure 3-10) shows absorption bands at (3031 $\text{cm}^{-1}$ ) to (aromatic C-H stretching), (2923,2826)  $\text{cm}^{-1}$  to aliphatic C-H) , (1612,1488)  $\text{cm}^{-1}$  to (C=C) ring, (1788,1735 $\text{cm}^{-1}$ ) to (C=O imide), (1373 $\text{cm}^{-1}$ ) to (C-N) , and (1002  $\text{cm}^{-1}$ ) to (C-Cl).

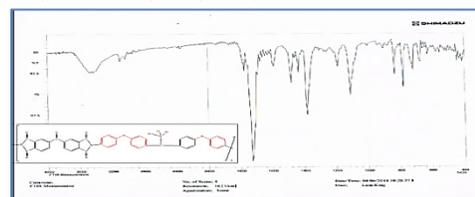
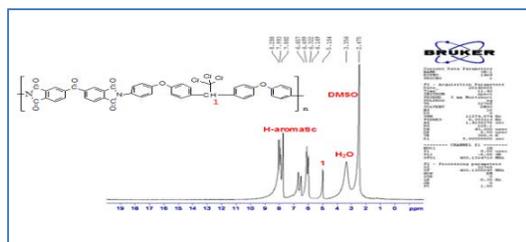


Fig 3.10 FTIR spectrum of (P2).

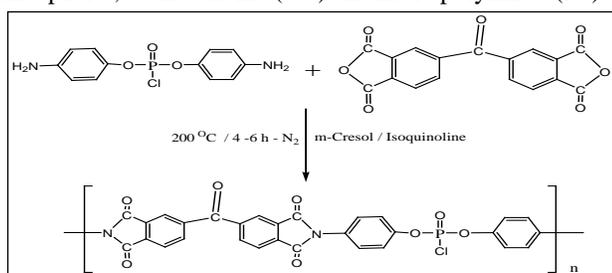
#### $^1\text{H NMR}$ spectrum of (P2)

$^1\text{H-NMR}$  spectrum of (**P2**) in (Figure 3-11) shows a multiplet at (6.16-8.20  $\delta$  ppm) to (22H, phenyl rings). a singlet at (5.27  $\delta$  ppm) to (1H,  $\text{C}_1$ ).


 Fig 3.11 :  $^1\text{H-NMR}$  spectrum of (P4)

### 3.2.3 Synthesis and Characterization of (P3).

Aromatic polyimide (P3) were prepared by polycondensation of equimolar an (BACP) with (BTDA) at 200 °C for (4-6 hrs.) in the presence of( isoquinoline) as catalytic and( m-Cresol) as solvent under a dry nitrogen atmosphere , as in Scheme (3-9) Aromatic polyimide (P3).



Scheme 3.9 : Synthesis of P3

### Characterization of (P3) IR-Spectra.

The FTIR spectrum of (P3) (Figure 3.12) shows absorption bands at (3031 $\text{cm}^{-1}$ ) to (aromatic C-H stretching), , (1669,1519)  $\text{cm}^{-1}$  to (C=C) ring, (1782,1712 $\text{cm}^{-1}$ ) to (C=O imide), (1342 $\text{cm}^{-1}$ ) to (C-N) , and (1388  $\text{cm}^{-1}$ ) to (P=O).

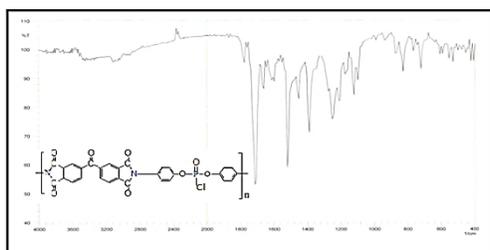
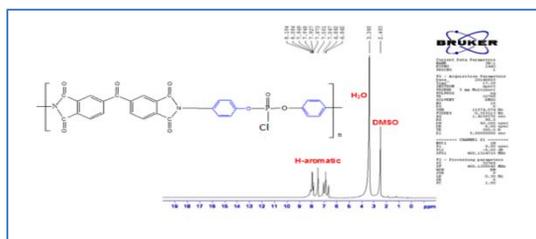


Fig 3.12: FTIR spectrum of (P3).

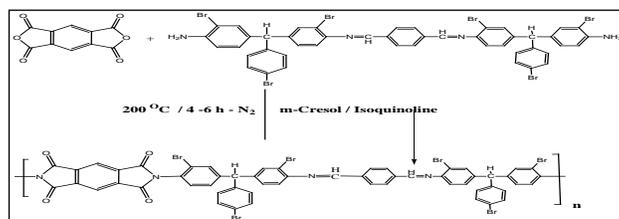
### $^1\text{H NMR}$ spectrum of (P3)

$^1\text{H-NMR}$  spectrum of (P3) in (Figure 3-13) shows a multiplet at (6.86-8.10  $\delta$  ppm) to (14H, phenyl rings). a singlet at (3.30  $\delta$  ppm) to ( $\text{H}_2\text{O}$ ).


 Fig 3.13 :  $^1\text{H-NMR}$  spectrum of (P3)

### 3.2.4 Synthesis and Characterization of (P4).

Aromatic polyimide (P4) were prepared by polycondensation of equimolar an (SB1) with (PMDA) at 200 °C for (4-6 hrs.) in the presence of( isoquinoline) as catalytic and( m-Cresol) as solvent under a dry nitrogen atmosphere , as in Scheme (3-10) Aromatic polyimide (P4).



Scheme 3.10 : Synthesis of P4

### Characterization of (P4) IR-Spectra.

The FTIR spectrum of (P4) (Figure 3-14) shows absorption bands at (3093 $\text{cm}^{-1}$ ) to (aromatic C-H stretching), , (1581,1473)  $\text{cm}^{-1}$  to (C=C) ring, (1774,1720 $\text{cm}^{-1}$ ) to (C=O imide), (1380 $\text{cm}^{-1}$ ) to (C-N) , and (1558  $\text{cm}^{-1}$ ) to (C=N).

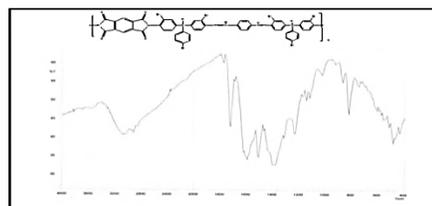
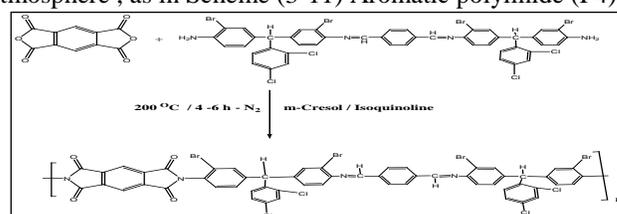


Fig 3.14: FTIR spectrum of (P4).

### 3.2.5 Synthesis and Characterization of (P5).

Aromatic polyimide (P5) were prepared by polycondensation of equimolar an (SB2) with (PMDA) at 200 °C for (4-6 hrs.) in the presence of( isoquinoline) as catalytic and( m-Cresol) as solvent under a dry nitrogen atmosphere , as in Scheme (3-11) Aromatic polyimide (P4).



Scheme 3.11 : Synthesis of P4

### Characterization of (P5) IR-Spectra.

The FTIR spectrum of (P5) (Figure 3-15) shows absorption bands at (3083 $\text{cm}^{-1}$ ) to (aromatic C-H stretching), , (1588,1473)  $\text{cm}^{-1}$  to (C=C) ring, (1687,1695 $\text{cm}^{-1}$ ) to (C=O imide), (1387 $\text{cm}^{-1}$ ) to (C-N) , and (1555  $\text{cm}^{-1}$ ) to (C=N).

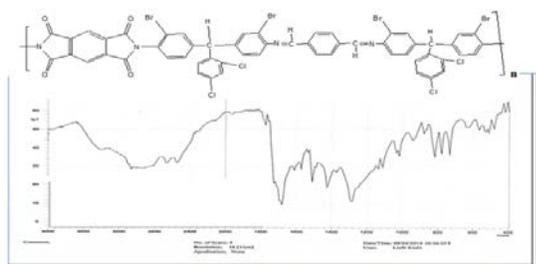


Fig 3.15: FTIR spectrum of (P5).

### 3.2 Thermal analysis of Aromatic polyimides.

(TGA) can serve as a useful indicator of polymer decomposition and flammability behavior. It is the most favored technique for rapid evaluation in comparing and ranking the thermal stability of various polymer. The thermal properties of the prepared aromatic polyimides were investigated by means of Thermo gravimetric analysis (TGA) in argon atmosphere at a heating rate of 10°C/min[27]. The results such as  $T_i$ ,  $T_{op}$ ,  $T_f$ ,  $T_{50\%}$ , % Residue at 800 °C, and char yields at 500°C are summarized in (Table 3.2). The polymers (P1,P2,P3,P4,P5) show slight weight loss around 380°C to 500°C while the temperatures from 500°C to 800°C show increases in the weight loss. The polymers

(PSPM,PSBT) around 220°C until 800°C show the increment in weight loss. The temperatures of 50% ( $T_{50\%}$ ) weight loss of (P1-P5) as a standard indication for thermal stability of polymers were all above 800°C. The polymers (PSPM,PSBT) show  $T_{50\%}$  around 546 °C to 582°C increases in weight loss. The char yields of (P1-P5) at 500°C are 85% to 65%, which indicate they could meet high temperature resistant requirements as some special materials in modern aerospace. In comparison to the polymers (PSPM,PSBT) have char yields (53% until 56%). The weight residue of (P1-P5) at 800°C are highest for any aromatic polyimide of this series, (53% until 56%). The polymers (PSPM,PSBT) around (38% until 42%) have the weight residue at 800°C. As already mentioned that in TGA analysis, particularly char yields, are a useful indication of polymer flammability and their trend to form protective barriers through formation of carbonations at high temperature, this can subsequently result in the generation of cross-linked or carbonized structures. with the carbonized residues, in char formation. This carbonized layer (char) isolates and protects the polymer from the flames. The flame retardant effect on thermal stability of the modified polymers are studied with (TGA) as shown is Figure(3-18), (3-19), (3-20), (3-21), (3-22)

TABLE 3.2  
THERMAL BEHAVIOR DATA OF AROMATIC POLYIMIDES

Aromatic Polyimides				DT/°C				$T_{50\%}$	Residue at °C800	Char % at 500°C
				$T_i$	$T_{op1}$	$T_{op2}$	$T_f$			
P1				380	525	-	>800	>800	60%	81%
P2				350	380	580	>800	>800	57%	77%
P3	480	450	-	>800	>800		66%		85%	
P4	355	480	567	>800	>800		50%		75%	
P5	350	460	498	>800	>800		53%		72%	

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.

Char% at 500°C : Residual weight percentage at 500°C in

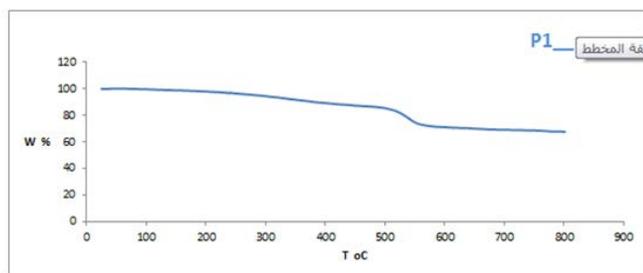


Figure 3-18: TGA curve of (P1)

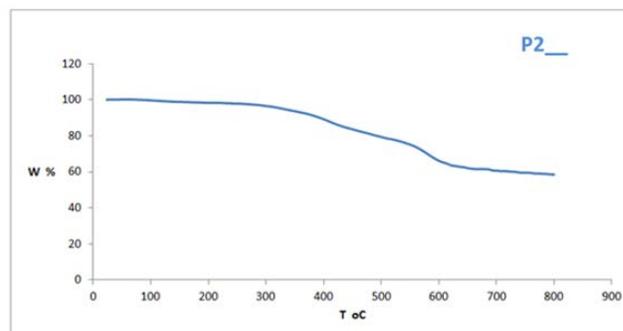


Figure 3-19: TGA curve of (P2)

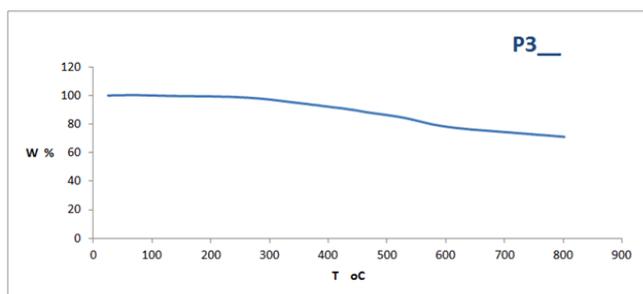


Figure 3-20: TGA curve of (P3)

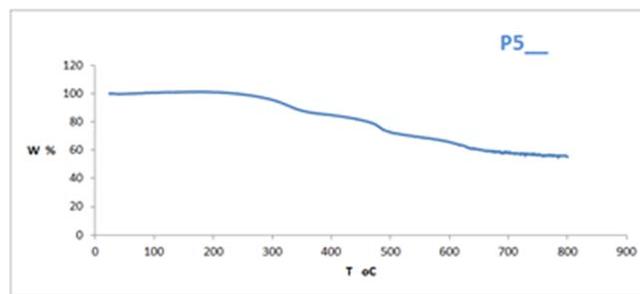


Figure 3-20: TGA curve of (P5)

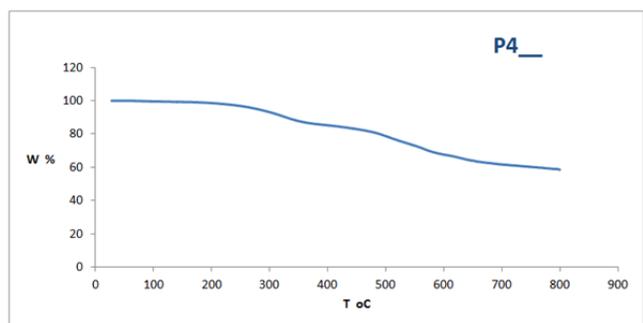


Figure 3-21: TGA curve of (P4)

### 3.3 Solubility of Aromatic polyimides

Solubility of polyimides [P1–P5] was qualitatively tested in some organic solvents and the results are summarized in (Table 3-3). The solubility was investigated as (0.01gm) of polymeric sample in (2ml) of a solvent. All of the newly synthesized aromatic polyimides were readily good soluble in common dipolar aprotic solvents including DMF, DMAC, NMP, DMSO and better solubility in m-Cresol without need for heating. Presence of ether linkages, and alkyl group caused improving of the solubility[28]. One of the major objectives of this study was producing modified aromatic polyimides with improved solubility. Presence of carbonyl of BTDA in derived aromatic polyimides increases solubility in comparison with rigid PMDA. This differences in solubility can be attributed to the molecular asymmetry, which inhibit close packing and reduce the inter chain interaction to enhance solubility.

Table 3-3 : Solubility of Aromatic polyimides [ P<sub>1</sub> – P<sub>5</sub> ]TABLE 33  
SOLUBILITY OF AROMATIC POLYIMIDES [ P<sub>1</sub> – P<sub>5</sub> ]

Polymer	Solvent									
	DMAC	DMF	NMP	Benzen	m-Cresol	THF	Conc.NaOH	CH <sub>2</sub> Cl <sub>2</sub>	DMSO	Conc.H <sub>2</sub> SO <sub>4</sub>
P <sub>1</sub>	++	+++	++	-	+++	+ -	+ -	+	++	+++
P <sub>2</sub>	+++	+++	+++	-	+++	++	+	++	++	+++
P <sub>3</sub>	++	++	+++	-	+++	+ -	+ -	+	++	+++
P <sub>4</sub>	+++	++	+++	-	+++	++	+	++	+++	+++
P <sub>5</sub>	+++	+++	++	-	+++	++	++	++	+++	+++

+++ Full soluble ,++ soluble at room temperature; + soluble on heating; + -partially soluble ; - insoluble

## IV. CONCLUSIONS

Many improvements are made in this study for to obtain the best and optimum thermal stability and flame retardant by different additives , Families of halogen and phosphorus-containing aromatic diamines were successfully synthesized and used to prepared aromatic polyimides. These products were characterized using FTIR, NMR and thermal gravimetric analysis (TGA). The combination of soft –P–O– and –C–O– linkage in aromatic polyimides ,and hard aromatic groups in the amines monomers or polyimides rendered the aromatic polyimides with tunable flexibility so all of the newly synthesized aromatic polyimides were readily good soluble in dipolar aprotic solvents without need for heating. Thermal analyses (TGA) showed that the resultant Aromatic polyimides had a pronounced improvement in flame-

retardant property, but with slightly reduced thermal stability during early period of the degrading process. A halogen and phosphorus content of polymers components led to excellent flame retardancy ,demonstrated by the high char yield of nearly 85% at 800 oC under argon. It is also important to note that the factors contributing to the thermal properties were illustrated by the structural versatility of aromatic polyimides in this work.

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