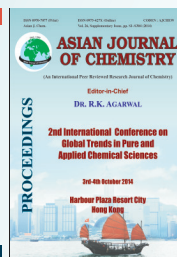




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Synthesis, Characterization, Thermal Properties and Flame Retardance of Aromatic Polyimides Containing Halogen and Phosphorus Components

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Several systematically varied aromatic polyimides were prepared by solution polycondensation reaction of different dianhydrides (pyromellitic dianhydride), 3,3',4,4'-benzophenone tetra-carboxylic dianhydride and 4,4'-hexafluoroisopropylidenebis(phthalic anhydride), with various structurally different diamines containing halogens and phosphorus components using a standard two-stage process with thermal imidization of poly(amic acid). Chemical structures, of these materials were characterized with FT-IR, NMR, elemental analysis. Thermal analysis of thermal gravimetric analysis (TGA) reveals that these resulted aromatic polyimides (P1-P4) possess thermal stability. Furthermore, high char yields in TGA analysis values indicate that these halogens and phosphorus containing aromatic polyimides possess excellent flame retardant properties.

Keywords: Aromatic polyimides, Pyromellitic dianhydride, 4,4'-Hexafluoroisopropylidenebis(phthalic anhydride).

INTRODUCTION

Polyimides belong to the important class of organic materials known as "high performance" polymers due to their exceptionally high thermo-oxidative stability, mechanical strength, electrical properties and high radiation and solvent resistance¹⁻³. So they are widely used in many applications as semiconductor devices, printed circuitry boards, *etc.*, they are condensation polymers incorporating the imide group CO-N-CO in their repeating units either as open chain or as rings and are generally derived from the reaction of organic diamines with organic tetra-carboxylic acids or their dianhydride⁴. Several methods have been developed for the preparation of polyimides, few of them are⁵: (A) Polyimides by polycondensation of diamine and dianhydride; (B) Polyimides from dihalides and aromatic diimide; (C) Polyimides from diisocyanates. Polymerization of aromatic diamines and dianhydrides 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^{6,7}. Aromatic polyimides have been widely used in industry because of excellent properties in thermal stability, good chemical resistance and mechanical properties. But they have some disadvantages that most of aromatic polyimides were not dissolved in most organic solvents and were difficult to process due to intermolecular

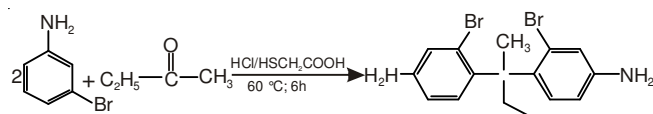
hydrogen bonding and their easy crystallization⁸. In order to improve solubility and processibility with maintaining thermal stability, it has been performed that some studies of introducing soft segments to the main chain of the polymers for example flexible ether and methylene groups into the polymer backbone, presence of carbonyl and hexafluoroisopropylidene groups in BTDA- and 6FDA-derived polyimides increased solubility in comparison with rigid PMDA-derived polyimide⁹. A most feasible approach for improving the flame retardant properties have been developed by incorporating additive- or reactive-type flame retardants into aromatic polyimides¹⁰ 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^{11,12}. Moreover, in the solid phase, the phosphorus-containing functional groups are converted by thermal decomposition to phosphoric acid¹³. 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 heat¹⁴. In this study is concerned with the synthesis and properties of new aromatic polyimides containing halogen and phosphorus compounds. The solubility, thermal stability were systematically investigated.

EXPERIMENTAL

m-Cresol, tetrahydrofuran (THF), phosphoryl chloride (POCl_3), 2-bromo aniline, dimethyl sulphoxide (DMSO), all from (Sigma-Aldrich, Germany). Iron powder, 3-bromo aniline, 4,4-diaminophenyl methane, 2,4-dichloro benzaldehyde, thioglycolic acid, pyromellitic dianhydride (PMDA) (Merck, Germany). Dichlorophenyl phosphine oxide, absolute methanol, ethyl methyl ketone, *N*-methyl-2-pyrrolidinone (NMP) (BDH, England). Dichloro-methane hydrochloric acid, absolute ethanol, *N,N*-dimethyl formamide (DMF), *p*-nitro phenol, triethylamine, isoquinoline, 4,4'-hexafluoroisopropylidene-bis(phthalic anhydride) (6FDA), 3,3',4',4'-benzophenone tetracarboxylic dianhydride (BTDA) were procured from elsewhere.

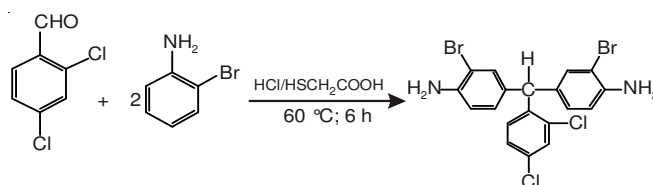
Synthesis of monomers

Synthesis of 4-(2-(4-amino-2-bromophenyl)butan-2-yl)-3-bromobenzenamine (ABBB): A mixture of 3-bromo aniline (61.2 g, 0.354 mol), ethyl methyl ketone (12.75 g, 0.177 mol), HCl catalyst (10 mL, 0.35 M) and thioglycolic acid (0.5 g, 6 mmol) 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 6 h. Then, the reaction mixture was transferred to cold water to quench the reaction mixture. The product was then filtered and dried under vacuum¹⁵. The product was dried and yield was 77 % of dark brown crystals, m.p. (187-190 °C) **Scheme-I**.



Scheme-I: Synthesis of ABBB

Synthesis of 4-(4-amino-3-bromophenyl)(2,4-dichlorophenyl)methyl)-2-bromobenzenamine (ABDB): This monomer was synthesized by the same way that (ABBB) is formed, using 2-bromo aniline (61.2 g, 0.354 mol) and 2,4-dichloro benzaldehyde (30.9 g, 0.177 mol) where yield 83 %, m.p. = 325 °C decomp. and colour is black **Scheme-II**.

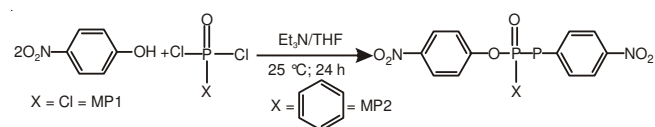


Scheme-II: Synthesis of ABDB

Synthesis of bis(4-nitro phenyl) chloro phosphonate (MP1): A 1 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_3) (56.8 g, 0.37 mol) in 200 mL of THF was added drop wise over a period of 30 min. 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. The solid was dried in a vacuum oven at 55 °C for 4 h to give 110.86 g (85 %) of white crystalline solid¹⁶, m.p. of 118-121 °C.

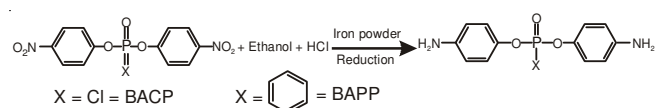
Synthesis of bis(4-nitro phenyl) phenyl phosphonate (MP2): This monomer was synthesized by the same way that (MP1) is formed, using materials (dichloro phenyl phosphine oxide) (148.1 g, 0.37 mol) and (4-nitrophenol) (102.9 g, 0.74 mol) where yield 83 %, m.p. = (190-193 °C) and color is light brown **Scheme-III**.



Scheme-III: Synthesis of MP1, MP2

Synthesis of bis(4-amino phenyl) chloro phosphonate (BACP): A (500 mL), 3 neck, round-bottom flask fitted with a mechanical stirrer, an addition funnel and a condenser, iron powder (8 g) was added portion wise with stirring to a hot mixture of (MP1) (5.96 g, 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 h at 78 °C. Upon cooling a dark brown precipitate formed, which was filtered off, washed with water, dried and recrystallized¹⁷. Yields: 60 %, m.p.: 295 °C.

Synthesis of bis(4-amino phenyl) phenyl phosphonate (BAPP): This monomer was synthesized by the same way that (MP24) is formed, using (MP2) (8.8 g, 0.02 moles). Yield 70 %, m.p. = (250-253 °C) and color is dark brown **Scheme-IV**.



Scheme-IV: Synthesis of BACP, BAPP

Synthesis of polymers: A 500 mL 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 (10 mL) *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 h¹⁸ (Table-1), **Scheme-V**.

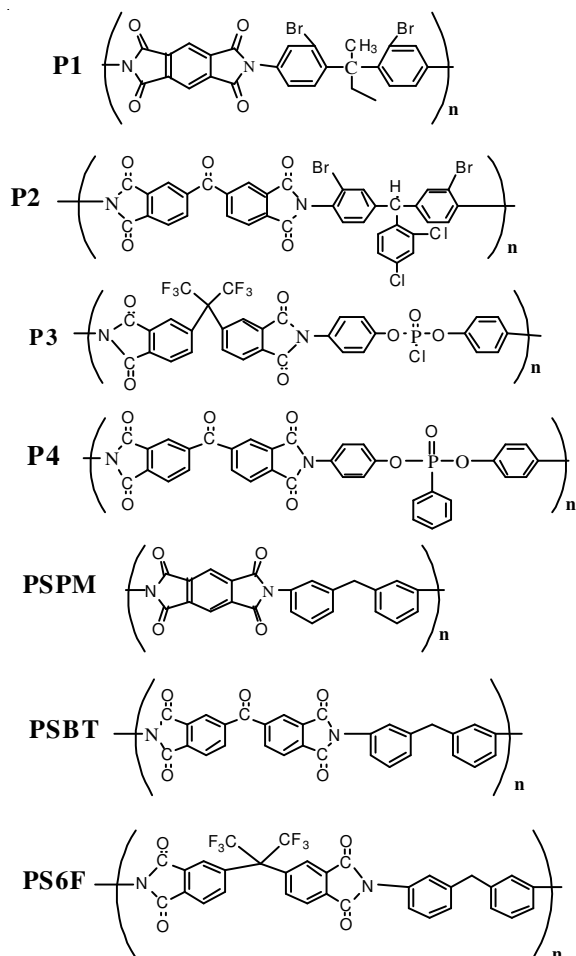
RESULTS AND DISCUSSION

¹H NMR spectrum of ABBB: ¹H NMR spectrum of ABBB shows a singlet at (0.87 δ ppm) to (3H, CH₃, C₁), a singlet at (1.48 δ ppm) to (3H, CH₃, C₂) a singlet at (1.76 δ ppm) to (2H, CH₂, C₃) a multiplet at (7.3-7.5 δ ppm) to (6H, phenyl rings) and a singlet at (9.5 δ ppm) to (4H, NH₂).

TABLE-1
 SYNTHESIS AND PHYSICAL PROPERTIES OF AROMATIC POLYIMIDES

Aromatic polyimides	Monomers		Dianhydride (g/1.4 mmol)	Aromatic diamine (g/1.4 mmol)	Yield (% wt)	Color
	Dianhydride	Aromatic diamine				
P1	PMDA	ABBB	0.305	0.550	83	Brown
P2	BTDA	ABDB	0.451	0.700	87	Light yellow
P3	6FDA	BACP	0.621	0.417	85	White
P4	BTDA	BAPP	0.451	0.476	80	Dark brown
PSPM	PMDA	4,4-Diamino phenylmethane	0.305	0.277	78	Light brown
PSBT	BTDA	4,4-Diamino phenylmethane	0.451	0.277	80	Deep brown
PS6F	6FDA	4,4-Diamino phenylmethane	0.621	0.277	83	White

Pyromellitic dianhydride (PMDA); 3,3',4,4'-benzophenone tetra-carboxylic dianhydride (BTDA); 4,4'-Hexafluoroisopropylidenebis(phthalic anhydride) (6FDA)



Scheme-V: Repeating units of aromatic polyimides

The FT-IR spectrum of (ABBB) shows absorption bands at (3332, 3209 cm^{-1}) to (NH_2), (3031 cm^{-1}) to (aromatic C-H stretching), (2885, 2823) cm^{-1} to aliphatic C-H, (1627, 1434) cm^{-1} to (C=C) ring, (1311 cm^{-1}) to (C-N) and (1010 cm^{-1}) to (C-Br).

^1H NMR spectrum of ABDB shows a singlet at (5.21 δ PPM) to (1H, C_1) a multiplet at (7.1-8.9 δ ppm) to (9H, phenyl rings) and a singlet at (10.1 δ ppm) to (4H, NH_2).

The FT-IR spectrum of ABDB absorption bands at (3394, 3247 cm^{-1}) to (NH_2), (3085 cm^{-1}) to (aromatic C-H stretching), (2939, 2846) cm^{-1} to aliphatic C-H, (1589, 1488) cm^{-1} to (C=C) ring, (1342 cm^{-1}) to (C-N), (1010 cm^{-1}) to (C-Br) and (1046 cm^{-1}) to (C-Cl).

The FTIR spectrum of **MP1** absorption bands at (3085 cm^{-1}) to (aromatic C-H stretching), (1612, 1488) cm^{-1} to (C=C) ring, (1350 cm^{-1}) to (NO_2), (1311 cm^{-1}) to (P=O), (1164 cm^{-1}) to (P-O) and (547 cm^{-1}) to (P-Cl).

Synthesis and characterization of BACP, BAPP: The catalytic hydrogenation of nitro group in the (MP1 to amino compound BACP) and (MP2 to amino compound BAPP) was accomplished by using ethyl alcohol and concentrated hydrochloric acid catalytic amount of iron powder as reducing agent at 78 $^\circ\text{C}$ for 6 h¹⁷.

^1H NMR spectrum¹⁹ of (BACP) a singlet at (3.3 δ PPM) to (H_2O), a multiplet at (6.4-6.5 δ ppm) to (8H, phenyl rings) and a singlet at (8.6 δ ppm) to (4H, NH_2).

^1H NMR spectrum²⁰ of (BAPP) a multiplet at (6.45-7.49 δ ppm) to (13H, phenyl rings) and a singlet at (9.11 δ ppm) to (4H, NH_2).

In the FTIR spectrum of (BAPP), the characteristic absorptions of the nitro group disappeared and (-NH) stretching absorption bands of the amino group appeared at (3340, 3278 cm^{-1}).

Characterization of aromatic polyimides

^1H NMR spectrum of P1 a singlet at (0.92 δ ppm) to (3H, CH_3 , C_1), a singlet at (1.47 δ ppm) to (3H, CH_3 , C_2) a singlet at (1.67 δ ppm) to (2H, CH_2 , C_3) a multiplet at (7.17-8.67 δ ppm) to (8H, phenyl rings).

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

The FTIR spectrum of (**P2**) (Fig. 1) shows absorption bands at (3093 cm^{-1}) to (aromatic C-H stretching), (2923, 2893 cm^{-1}) to aliphatic C-H, (1581, 1473 cm^{-1}) to (C=C) ring, (1774, 1720 cm^{-1}) to (C=O imide), (1380 cm^{-1}) to (C-N), (1110 cm^{-1}) to (C-Br) and (1002 cm^{-1}) to (C-Cl).

The FTIR spectrum of (**P3**) absorption bands at (3085 cm^{-1}) to (aromatic C-H stretching), (1612, 1512 cm^{-1}) to (C=C) ring, (1782, 1720 cm^{-1}) to (C=O imide), (1411 cm^{-1}) to (C-N), (1110 cm^{-1}) to (C-O), (1257 cm^{-1}) to (P-O) and (1026 cm^{-1}) to (C-F).

^1H NMR spectrum of (**P4**)²⁰ a multiplet at (6.86-8.10 δ ppm) to (19H, phenyl rings).

The FTIR spectrum of (**P4**) absorption bands at (3031 cm^{-1}) to (aromatic C-H stretching), (1596, 1519 cm^{-1}) to (C=C)

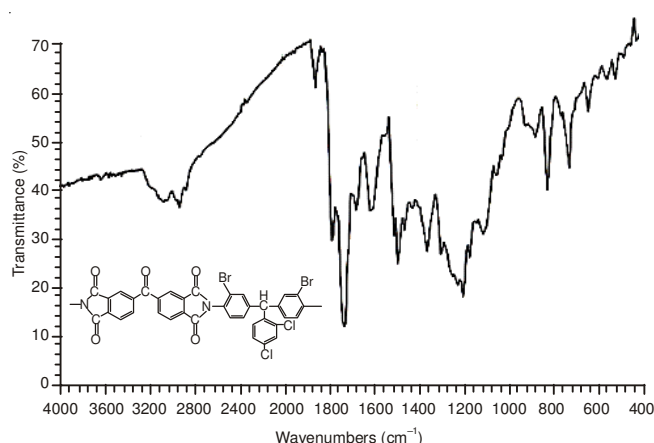


Fig. 1. FTIR spectrum of P2

ring, (1782, 1712 cm^{-1}) to (C=O imide), (1342 cm^{-1}) to (C-N), (1118 cm^{-1}) to (C-O), (1249 cm^{-1}) to (P-O) and (1388 cm^{-1}) to (P=O).

Thermal analysis of aromatic polyimides: Thermogravimetric analysis can serve as a useful indicator of polymer decomposition and flammability behaviour. 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 thermogravimetric analysis in argon atmosphere at a heating rate of 10 $^{\circ}\text{C}/\text{min}$. The results such as T_i , T_{op} , T_f , $T_{50\%}$, % residue at 800 $^{\circ}\text{C}$ and char yields at 500 $^{\circ}\text{C}$ are summarized in (Table-2). The polymers (P1, P2, P3, P4) show slight weight loss around 340 to 500 $^{\circ}\text{C}$ while the temperatures from 500 to 800 $^{\circ}\text{C}$ show increases in the weight loss. The polymers (PSPM, PSBT, PS6F) around 220 $^{\circ}\text{C}$ until 800 $^{\circ}\text{C}$ show the increment in weight loss^{6,21}. The temperatures of 50 % ($T_{50\%}$) weight loss of (P1-P4) as a standard indication for thermal stability of polymers were all above 800 $^{\circ}\text{C}$. The

polymers (PSPM, PSBT, PS6F) show $T_{50\%}$ around 490 to 590 $^{\circ}\text{C}$ increases in weight loss. The char yields of (P1-P4) at 500 $^{\circ}\text{C}$ are 86 to 91 %, which indicate they could meet high temperature resistant requirements as some special materials in modern aerospace. In comparison to the polymers (PSPM, PSBT, PS6F) have char yields (48 % until 56 %). The weight residue of (P1-P4) at 800 $^{\circ}\text{C}$ are highest for any aromatic polyimide of this series, (67 % until 85 %). The polymers (PSPM, PSBT, PS6F) around (20 % until 42 %) have the weight residue at 800 $^{\circ}\text{C}$. 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.

Solubility of aromatic polyimides²²: Solubility of polyimides [P1-P4] was qualitatively tested in some organic solvents and the results are summarized in (Table-3). The solubility was investigated as (0.01 g) of polymeric sample in (2 mL) 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. One of the major objectives of this study was producing modified aromatic polyimides with improved solubility. Presence of carbonyl and hexa fluoro isopropylidene groups of BTDA and 6FDA in derived aromatic polyimides increases solubility in comparison with rigid PMDA. This differences insolubility can be attributed to the molecular asymmetry and presence of bulky CF_3 groups, which inhibit close packing and reduce the inter chain interaction to enhance solubility.

TABLE-2
THERMAL BEHAVIOR DATA OF AROMATIC POLYIMIDES

Aromatic polyimides	DT ($^{\circ}\text{C}$)				$T_{50\%}$	Residue at $^{\circ}\text{C}$ 800	Char % at 500 ($^{\circ}\text{C}$)
	T_i	T_{op1}	T_{op2}	T_f			
P1	380	525	---	> 800	> 800	67 %	86 %
P2	450	570	---	> 800	> 800	73 %	88 %
P3	435	580	---	> 800	> 800	79 %	91 %
P4	440	550	---	> 800	> 800	80 %	94 %
PSPM	320	440	510	> 800	546	42 %	56 %
PSBT	220	330	410	> 800	582	38 %	53 %
PS6F	240	290	370	> 800	492	20 %	48 %

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 $^{\circ}\text{C}$: Residual weight percentage at 500 $^{\circ}\text{C}$ in Argon by TGA

TABLE-3
SOLUBILITY OF AROMATIC POLYIMIDES [P₁-P₄]

Polymer	Solvent									
	DMAC	DMF	NMP	Benzen	<i>m</i> -Cresol	THF	Conc. NaOH	CH_2Cl_2	DMSO	Conc. H_2SO_4
P ₁	++	+++	++	-	+++	+-	+-	+	++	+++
P ₂	+++	+++	+++	-	+++	++	+	++	++	+++
P ₃	++	++	+++	-	+++	+-	+-	+	++	+++
P ₄	+++	++	+++	-	+++	++	+	++	+++	+++

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

Conclusion

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. 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 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 99 % at 500 °C 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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