

Synthesis and Characterization of New Flame-Retardant Poly(amide-imide)s Containing Phosphine Oxide and Hydantoin Moieties in the Main Chain

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ABSTRACT: Six new flame-retardant poly(amide-imide)s (PAIs) **9a–f** with high inherent viscosities containing phosphine oxide and hydantoin moieties in main chain were synthesized from the polycondensation reaction of *N,N'*-(3,3'-diphenylphenylphosphine oxide) bistrimellitamide diacid chloride **7** with six hydantoin derivatives **8a–f** by two different methods such as solution and microwave assisted polycondensation. Results showed that the microwave assisted polycondensation, by using a domestic microwave oven, proceeded rapidly, compared with solution polycondensation, and was completed in about 7–9 min. All of the obtained polymers were fully characterized by means of elemental analysis, viscosity measurements, solubility test, and FTIR spectroscopy.

Thermal properties and flame retardant behavior of the PAIs **9a–f** were investigated using thermal gravimetric analysis (TGA and DTG) and limited Oxygen index (LOI). Data obtained by thermal analysis (TGA and DTG) revealed that these polymers showed good thermal stability. Furthermore, high char yields in TGA and good LOI values indicated that these polymers are capable of exhibiting good flame retardant properties. These polymers can be potentially utilized in flame retardant thermoplastic materials. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 102: 5062–5071, 2006

Key words: flame-retardant polymers; phosphine oxide moieties; hydantoin moieties; limited Oxygen index

INTRODUCTION

During earlier decades, conventional materials such as metals, wood, glass, and ceramic have been increasingly replaced by synthetic polymers, because of their versatility, low density, good mechanical and physical properties, and easy molding process.^{1,2} However, these advantages of polymeric materials are shadowed by easy fire catching and low stability in high temperatures in comparison with metals. Hence, in the last few years considerable attention has been paid for preparing flame retardant polymers.^{3,4} Many flame retardant polymers have been developed and among these, phosphorus containing polymers are the most widely used.^{5–9} The general types of phosphorus moieties have been incorporated into different polymeric backbones such as epoxy resin, poly(amic-acid), polycarbonate, poly(vinyl chloride), polyester, polyimide, and poly(methyl methacrylate).^{10–16} Among the polymers containing phosphorus groups, the polymers

with phosphine oxide moieties have major advantages, such as good flame retardant properties, high thermal oxidative stability, enhanced solubility in organic solvents, improved miscibility, and good adhesion to other compounds.^{10,17–19}

Recently, there has been growing interest in applying microwave energy to synthetic organic chemistry,^{20–22} for sample preparation for analysis,²³ extraction of natural products from plants,²⁴ waste treatment,²⁵ and polymer synthesis.^{26,27} The reactions are very fast and are completed within a short period time. Recently, we have used microwave irradiation for the synthesis of poly(amide-imide)s (PAIs) and poly(ester-imide)s.^{28–32}

In this article, six new flame retardant PAIs **9a–f** were prepared by polycondensation reaction between bis(3-aminophenyl) phenyl phosphine oxide diacid chloride **7** with hydantoin **8a**, 5,5-dimethyl hydantoin **8b**, 5-ethyl-5-methyl hydantoin **8c**, 5,5-diethyl hydantoin **8d**, 5-spirocyclopentyl hydantoin **8e**, and 5-spirocyclohexyl hydantoin **8f** by two different methods such as solution and microwave assisted polycondensation. These polymers have phosphine oxide moieties in main chain and shows flame retardant behavior. These properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics.

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EXPERIMENTAL

Materials

All chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI), and Merck Chemical Co. (Germany).

Techniques

^{13}C NMR spectra (500 MHz) were recorded on a Bruker advanced 500 instrument (Germany). Fourier transform infrared (FTIR) spectra were recorded on Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were obtained using KBr pellets. Vibrational transition frequencies are reported in wavenumber (cm^{-1}). Band intensities are assigned as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosities were measured by a standard procedure using a Technico Regd. Trad Mark Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were taken on a Mettler TA4000 System under N_2 atmosphere at a rate of $10^\circ\text{C}/\text{min}$. Limited Oxygen index (LOI) was measured on a Stanton Redcraft flame meter. Elemental analyses were performed by the Arak Petrochemical Company,

Arak, Iran. A Samsung domestic microwave oven (2450 MHz, 900 W) was used for carrying out polycondensation reactions.

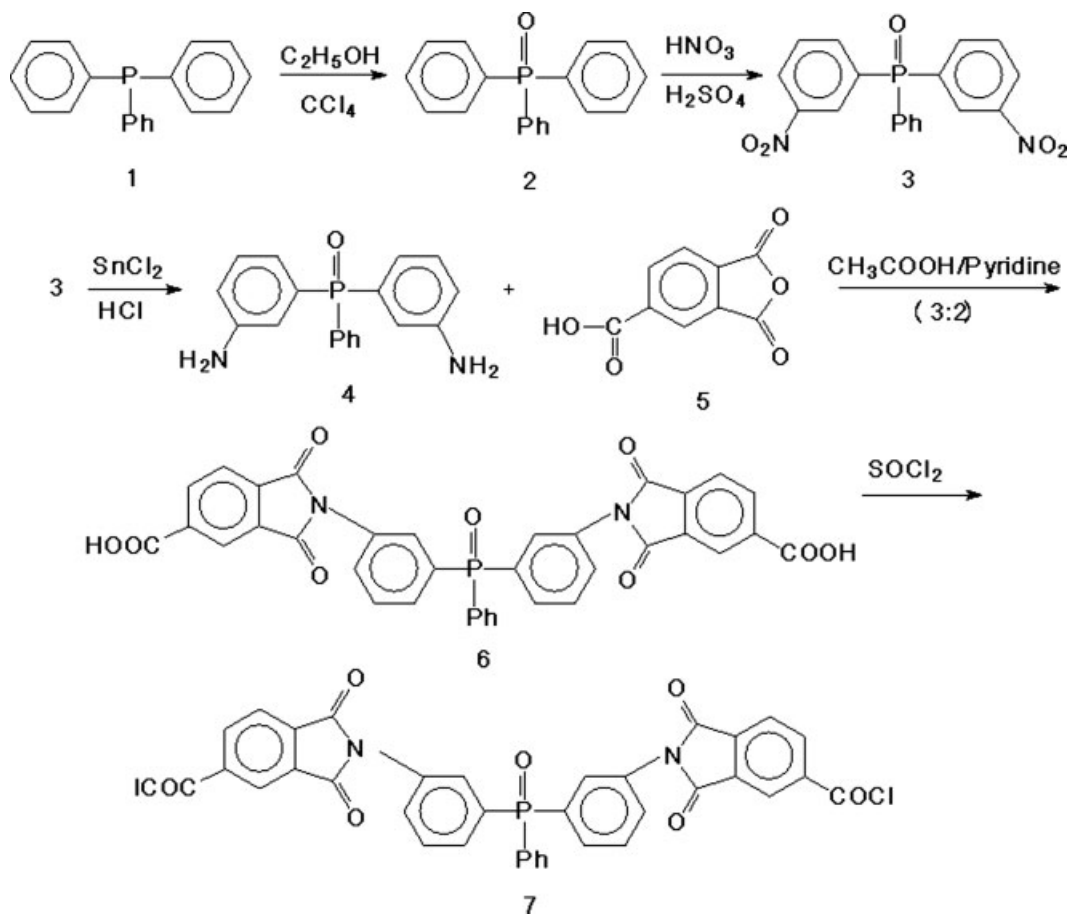
Monomer synthesis

N,N'-(3,3'-Diphenylphenylphosphine oxide) bistrimellitimidic acid chloride 7

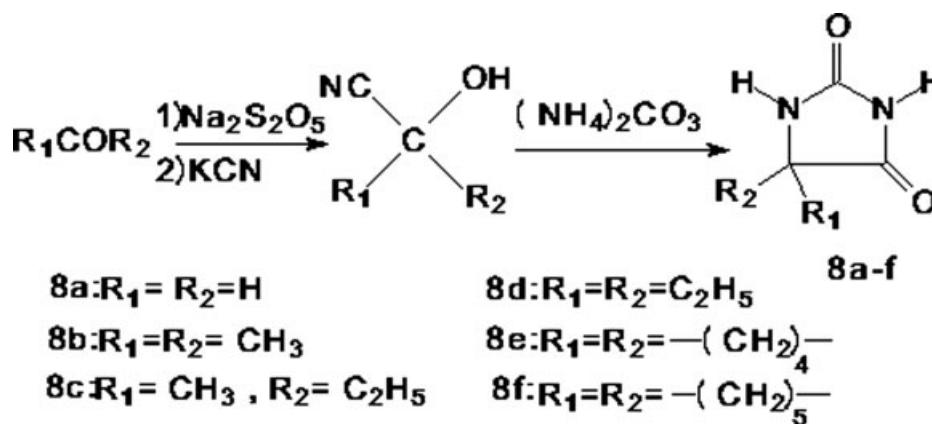
This compound was prepared according to a typical procedure shown in Scheme 1.

Triphenyl phosphine oxide 2

Into a 100-mL round-bottomed flask 4.94 g (20 mmol) of triphenyl phosphine 1, 12 mL of absolute ethanol, 20 mL of tetrachloromethane, and a stirring bar were placed. The mixture was refluxed for 4 h. Then the solvent was removed under reduced pressure and the residue was added to 100 mL of cold water. A white crystalline substance was formed. The precipitate was then filtered off and dried to give 4.24 g (81%) of compound 2. mp $154\text{--}156^\circ\text{C}$. FTIR (KBr): 3074 (m), 3038 (m), 1674 (m), 1589 (m), 1483 (m), 1437 (s), 1180 (s), 1118 (s, br), 997 (w), 854 (w), 721 (s, br), 696 (s) cm^{-1} .



Scheme 1



Scheme 2

Bis(3-nitrophenyl) phenyl phosphine oxide 3

Into a 250-mL round-bottomed flask equipped with a stirrer 27.8 g (100 mmol) of triphenyl phosphine oxide 2 and a mixture of 200 mL of 96% sulfuric acid were placed. The reactant was dissolved and the reaction system was then cooled to -5°C with ice/salt bath. Then a solution of 14.5 g (22 mmol) of fuming nitric acid in 100 mL of sulfuric acid was added in a drop-wise manner for 2 h, and the reaction system was maintained at room temperature for further 8 h. The reaction solution was then hydrolyzed over 2 L of ice. After the ice had melted, the mixture was extracted with chloroform and washed with aqueous sodium bicarbonate solution until neutral pH was achieved and the solvent was removed. Finally, the solid residue was

recrystallized with absolute ethanol and then 25.70 g (70%) of yellow crystals of bis(3-nitrophenyl) phenyl phosphine oxide 3 was obtained. mp $245\text{--}248^\circ\text{C}$. FTIR (KBr): 3082 (m), 2924 (w), 2882 (w), 1674 (w), 1608 (w), 1523 (s), 1467 (w), 1346 (s), 1278 (m), 1197 (s), 1140 (m), 1095 (m), 881 (m), 731 (m), 675 (s) cm^{-1} .

Bis(3-aminophenyl) phenyl phosphine oxide 4

Bis(3-nitrophenyl) phenyl phosphine oxide 3 (15.4 g, 50 mmol) was added into a 500-mL round-bottomed flask with 144 g of powdered tin(II) chloride dihydrated to which a solution of 160 mL fuming hydrochloric acid in 320 mL ethanol was added. The reaction mixture was stirred at room temperature for 5 h, after

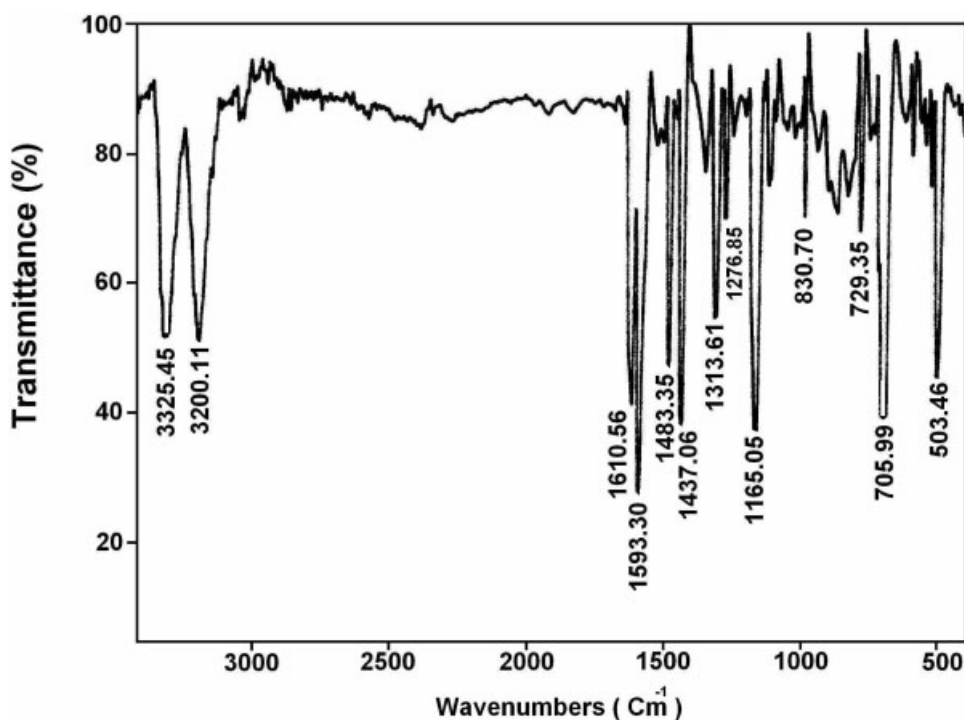


Figure 1 FTIR spectrum of diamine 4.

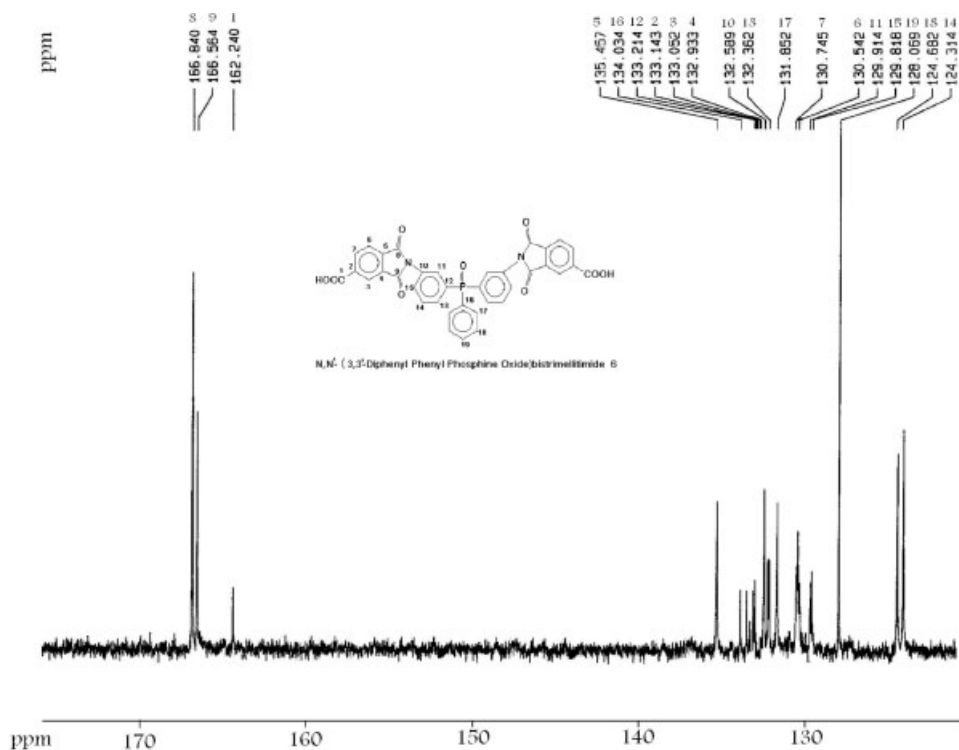


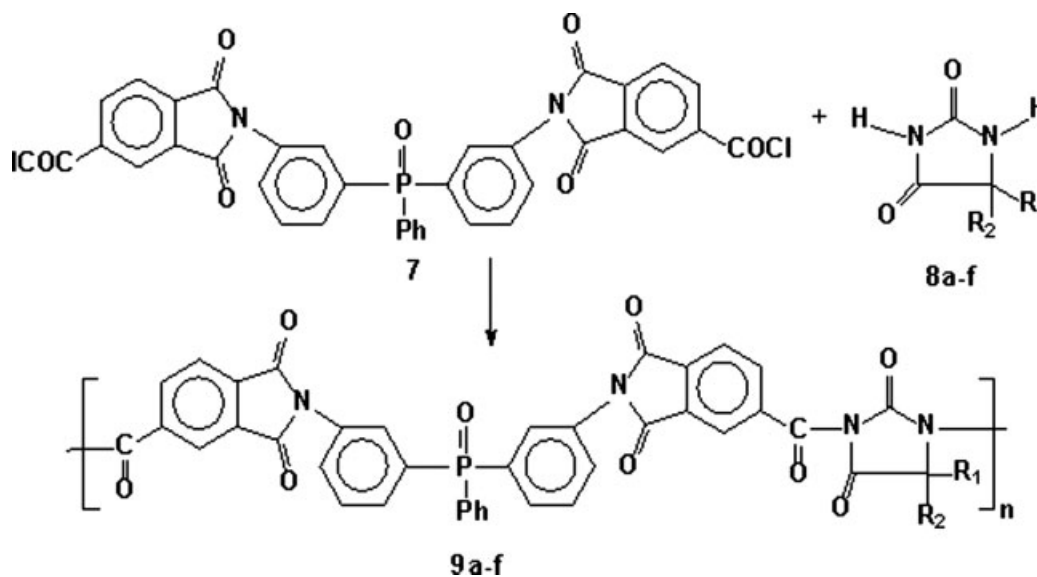
Figure 2 ^{13}C NMR spectrum of imide acid 6.

which the solution was concentrated and then neutralized by a 25% aqueous NaOH solution. The obtained solution was then extracted with chloroform and the organic layer was collected and concentrated under reduced pressure. Finally, the obtained solid was dried under reduced pressure and then 9.41 g (73%) of yellow crystals of bis(3-aminophenyl) phenyl phosphine oxide 4 was obtained. mp 115–117°C. FTIR (KBr): 3325 (m), 3200 (m), 3070 (w), 1630 (m), 1593 (s), 1483 (m),

1437 (s), 1313 (m), 1276 (w), 1165 (s), 830 (w), 729 (m), 705 (s), 503 (m) cm^{-1} . Anal. calcd for $\text{C}_{18}\text{H}_{17}\text{N}_2\text{OP}$: C, 70.12; H, 5.56; N, 9.09. Found: C, 69.71; H, 5.64; N, 8.91.

N,N'-(3,3'-Diphenylphenyl phosphine oxide) bistrimellitamide 6

Into a 250-mL round-bottomed flask 5.0 g (16 mmol) of bis(3-aminophenyl) phenyl phosphine oxide 4, 7.3 g



Scheme 3

TABLE I
Synthesis and Some Physical Properties of
PAIs 9a–f by Microwave Irradiation

Hydantoins	Polymer	Yield (%)	Time (min) ^a	η_{inh} (dL/g) ^b
8a	9a	90	7	1.20
8b	9b	92	8	1.15
8c	9c	96	9	1.30
8d	9d	91	9	1.40
8e	9e	95	8	1.50
8f	9f	92	9	1.50

^a Time of irradiation by microwave oven.

^b Measured at a concentration of 0.5g/dL in DMF at 25°C.

(32 mmol) trimellitic anhydride **5**, 80 mL mixture of acetic acid and pyridine (3:2), and a stirrer bar were placed. The mixture was stirred at room temperature overnight and was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was dissolved in 100 mL of cold water. Then 5 mL of concentrated HCl was added. The solution was stirred until a white yellow precipitate was formed. The precipitate was then filtered off and purified by recrystallization from DMF-H₂O solution and dried in vacuum to give 9.45 g (90%) of compound (**6**). mp 310–314°C. FTIR (KBr): 2700–3200 (m, br), 1780 (sh), 1724 (s, br), 1485 (m), 1425 (m), 1373 (s), 1219 (m), 750 (w), 727 (m) cm⁻¹. ¹³C NMR (DMSO-*d*₆, δ): 166.84, 166.56, 162.24, 135.45, 134.03, 133.21, 133.14, 133.05, 132.93, 132.58, 132.36, 131.85, 130.74, 130.54, 129.91, 129.81, 128.06, 124.68, 124.31 ppm. Anal. calcd for C₃₆H₂₁N₂O₉P: C, 65.86; H, 3.22; N, 4.26. Found: C, 65.7; H, 3.3; N, 4.0.

N,N'-(3,3'-Diphenylphenylphosphine oxide) bistrimellitimidic diacid chloride **7**

Into a 100-mL round-bottomed flask were placed 6.56 g (10 mmol) of *N,N'*-(3,3'-diphenylphenylphosphine oxide) bistrimellitimidic diacid chloride **6** and 40 mL of thionyl chloride. The mixture was heated in an oil bath up to 60°C until the suspension mixture was converted to a clear solution. Then, the solution was stirred overnight at room temperature. Unreacted thionyl chloride was removed under reduced pressure and the residue was washed with dry *n*-hexane twice and then the precipitate was filtered off and purified by recrystallization from THF and dried in vacuum to give 6.6 g (90%) of yellow crystals of compound **7**. mp 213–215°C. FTIR (KBr): 1795 (sh), 1742 (s, br), 1510 (m), 1431 (m), 1375 (s), 1221 (m), 753 (w), 729 (m) cm⁻¹. Anal. calcd for C₃₆H₁₉N₂O₇PCl₂: C, 62.34; H, 2.76; N, 4.03; P, 4.47. Found: C, 61.9; H, 2.9; N, 3.9; P, 3.8.

Hydantoin derivatives (8a–f)

Hydantoin derivatives (**8a–f**) were prepared according to a typical procedure shown in Scheme 2.²⁸

Polymer synthesis

Poly(amide-imide) **9a** was prepared from the reaction of *N,N'*-(3,3'-diphenylphenyl phosphine oxide) bistrimellitimidic diacid chloride **7** with hydantoin **8a** by two different methods.

Method A. Solution polycondensation with pyridine as a base: Into a 25-mL round-bottomed flask fitted with a stirring bar were placed 0.10 g (1.0 mmol) hydantoin **8a** and 9 mL of DMAc. The mixture was cooled in an ice-water bath, and 0.24 g (3.2 mmol) of pyridine was added to this solution. Then 0.69 g (1.0 mmol) *N,N'*-(3,3'-diphenylphenylphosphine oxide) bistrimellitimidic diacid chloride **7** was added all at once. The polymerization proceeded as the acid chloride was dissolved. The reaction mixture was stirred in an ice-water bath for 1 h. The cooling bath was removed, the stirring was continued at room temperature overnight, and then heated at 80°C for 12 h. The reaction mixture was poured into 50 mL of methanol. The precipitated polymer was collected by filtration, washed thoroughly with methanol, and dried at 80°C for 12 h under vacuum to leave 0.54 g (82%) of polymer **9a**.

Method B. Polymerization by microwave irradiation in a porcelain dish: An equimolar mixture of 0.69 g (1.0 mmol) *N,N'*-(3,3'-diphenylphenylphosphine oxide) bistrimellitimidic diacid chloride **7** and 0.10 g (1.0 mmol) hydantoin **8a** were placed in a porcelain dish and the mixture was ground until a fine powder formed. Then 1 mL of *o*-cresol was added to the mixture and mixed until a homogeneous solution formed. Then the reaction mixture was irradiated in a microwave oven at full power for 10 min. The reaction mixture was poured into 50 mL of methanol and the resulting polymer was filtered off and dried at 80°C for 12 h under vacuum to leave 0.69 g (96%) of solid polymer **9a**.

RESULTS AND DISCUSSION

Monomer synthesis

N,N'-(3,3'-Diphenylphenylphosphine oxide) bistrimellitimidic diacid chloride **7** was prepared in five steps

TABLE II
Synthesis and Some Physical Properties of PAIs
9a–f by Solution Polycondensation

Hydantoins	Polymer	Yield (%)	η_{inh} (dL/g) ^a
8a	9a	80	0.70
8b	9b	83	0.65
8c	9c	80	0.60
8d	9d	81	0.78
8e	9e	85	0.60
8f	9f	79	0.65

^a Measured at a concentration of 0.5g/dL in DMF at 25°C.

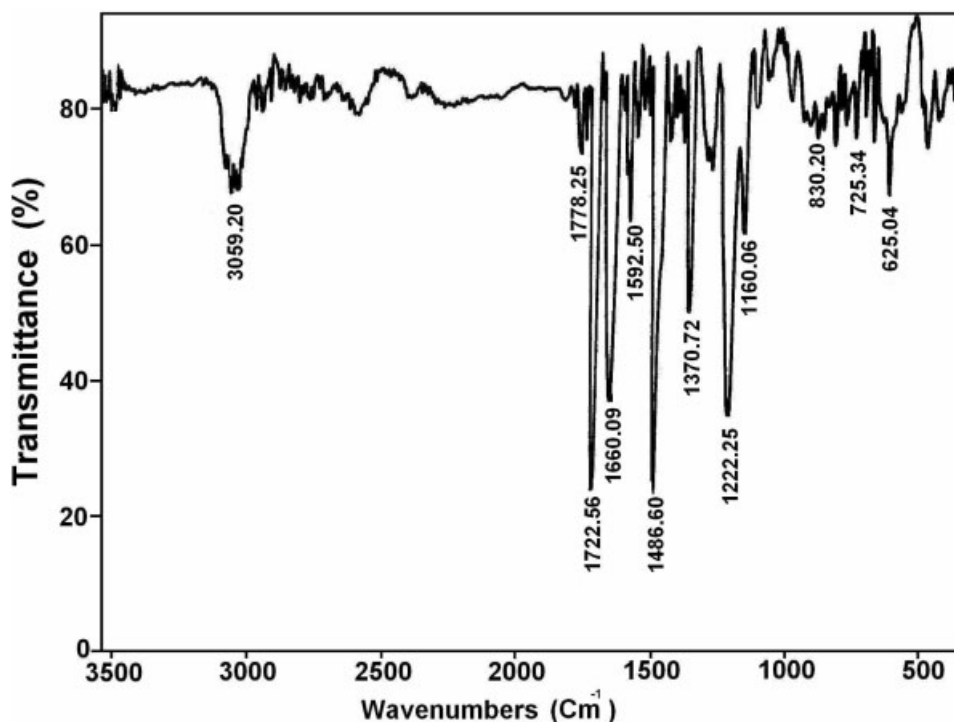


Figure 3 FTIR spectrum of PAI 9c.

from simple organic compounds such as triphenyl phosphine **1**, as shown in Scheme 1. At first, a diamine compound **4** with a phosphine oxide moiety was obtained. Then the diimide acid **6** was synthesized by condensation reaction of two equimolar amounts of trimellitic anhydride **5** with one equimolar amount of diamine compound **4** in a mixture of acetic acid–pyridine (3:2). After evaporating the solvent and dissolving the residue in cold water, a gum-like solid was obtained that breaks up under concentrated HCl and gives a white yellow solid when recrystallized with DMF–H₂O. Then the resulting diimide acid **6** was converted to its diacid chloride derivative **7** by reaction with excess thionyl chloride. The diimide-acid chloride **7** was purified by washing with *n*-hexane and recrystallized with extra-pure tetrahydrofuran.

The chemical structures and purities of diamine **4**, diimide acid **6**, and diimide acid chloride **7** were also analyzed by elemental analysis, ¹³C NMR, and FTIR

spectroscopy. The measured results in elemental analyses closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained. Figure 1 shows the FTIR spectra of bis(3-aminophenyl) phenyl phosphine oxide **4**. Peaks appearing at 3325 and 3200 cm⁻¹ indicate the existence of amine groups (N–H stretching vibration). Other peaks at 1165 (P=O) and 1437 cm⁻¹ (P–Ph) confirm the presence of phosphine oxide moiety in this compound. FTIR spectra of diimide acid **6** showed absorption bands at 2700–3200 (acid O–H stretching), 1780 (imide, asymmetric C=O stretching), 1724 (acid C=O and symmetric imide stretching), 1380 and 750 cm⁻¹ (imide characteristic ring vibration), confirming the presence of imide ring and carboxylic groups in this compound.

The ¹³C NMR spectra of diimide acid **6** show 19 signals, including 3 signals of carbon atoms associated with carbonyl groups (C₁) in carboxylic acid and imide rings (C₈, C₉) and 16 signals of carbon atoms present in

TABLE III
Elemental Analysis of Poly(amide-imide)s 9a–f

Polymer	Formula	C%		H%		N%	
		Calcd	Found	Calcd	Found	Calcd	Found
9a	C ₃₉ H ₂₁ N ₄ O ₉ P (720.39) _n	65.01	64.00	2.91	3.30	7.77	6.50
9b	C ₄₁ H ₂₅ N ₄ O ₉ P (748.41) _n	65.79	64.20	3.34	3.30	7.48	6.40
9c	C ₄₂ H ₂₇ N ₄ O ₉ P (762.42) _n	66.16	65.30	3.54	2.90	7.34	6.10
9d	C ₄₃ H ₂₉ N ₄ O ₉ P (776.43) _n	66.51	65.00	3.73	3.00	7.21	6.50
9e	C ₄₃ H ₂₇ N ₄ O ₉ P (774.43) _n	66.68	65.40	3.48	2.80	7.23	6.80
9f	C ₄₄ H ₂₉ N ₄ O ₉ P (788.44) _n	67.02	66.10	3.67	3.10	7.10	6.60

TABLE IV
Solubility of PAIs 9a–f

Solvent	9a	9b	9c	9d	9e	9f
H ₂ SO ₄	+	+	+	+	+	+
DMAc	+	+	+	+	+	+
DMSO	+	+	+	+	+	+
DMF	+	+	+	+	+	+
NMP	+	+	+	+	+	+
THF	–	–	–	–	–	–
CHCl ₃	–	–	–	–	–	–
Acetone	–	–	–	–	–	–
EtOH	–	–	–	–	–	–
MeOH	–	–	–	–	–	–

+, Soluble at room temperature; –, insoluble at room temperature.

aromatic rings (C_{2–7}, C_{10–19}) (Fig. 2). These peaks in ¹³C NMR spectra along with elemental analyses data confirm the proposed structure of compound 6.

In the FTIR spectra of compound 7 disappearance of a broad peak at 2700–3200 cm⁻¹ confirmed a complete conversion of diimide acid 6 to diimide-acid chloride 7. On the other hand, because of the electron withdrawing character of the Cl groups, two carbonyl peaks of the diimide-acid chloride 7, in comparison with starting diimide acid 7, were shifted to a higher frequency (1810 and 1760 cm⁻¹ in comparison with 1760 and 1720 cm⁻¹).

Hydantoins constitute an important class of heterocycles in medical chemistry because many derivatives have been identified that display interesting activities against a broad range of biological targets.³³ Hydantoin derivatives of 8a–f were synthesized by the Bucherer-Berg method. In this method hydantoin com-

pounds 8a–f were prepared by the reactions of proper cyanohydrin derivatives with ammonium carbonate (Scheme 2). In the previous papers we used hydantoin derivatives as difunctional monomers for synthesis of new polymers. We found that the introduction of hydantoin derivatives in polymer backbone increases solubilities in common organic solvents.^{34–38}

Polymer synthesis

PAIs 9a–f were synthesized by microwave assisted polycondensation as well as solution polycondensation reactions of an equimolar mixture of monomer 7 with six different derivatives of hydantoin 8a–f as shown in Scheme 3. The microwave-assisted polycondensation reactions were carried out in a porcelain dish in the presence of a small amount of *o*-cresol. *o*-Cresol was used as a polar organic medium that acts as a primary microwave absorber and as a solvent for both the starting monomers and the resulting polymers. This allows the reaction mixture to be uniformly heated and the subsequent polycondensation reaction leads to the high yield polymer formation. The optimum reaction times (irradiation time) were found to be between 7–9 min. Less than this time, the polymers obtained will have lower inherent viscosities, and more than this time, the materials will be degraded.

Polymer characterization

The reaction yields and some physical data of PAIs 9a–f that were obtained by microwave assisted polycondensation are listed in Table I. Furthermore, we compared this method with conventional solution

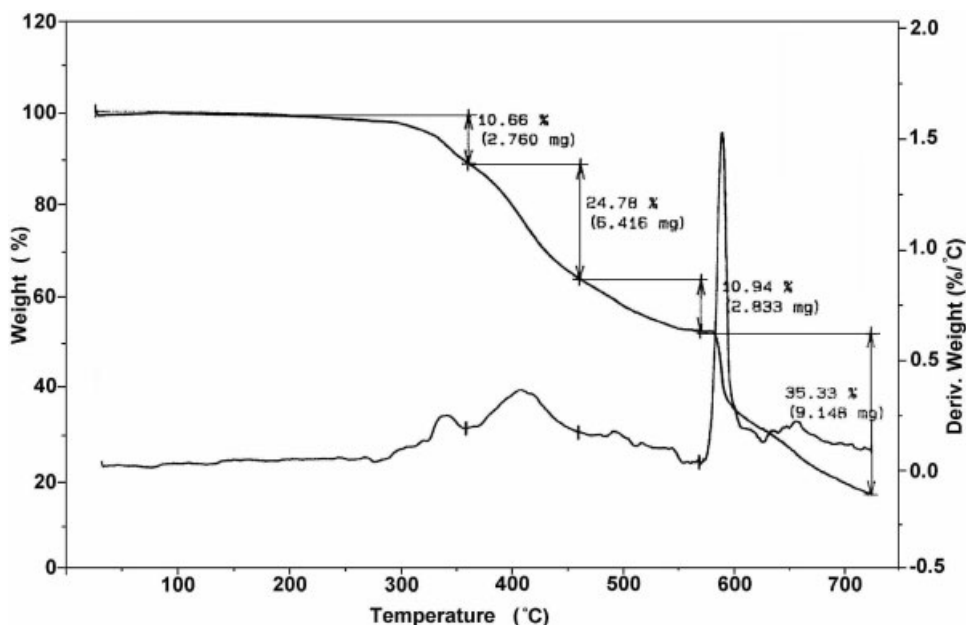


Figure 4 TGA and DTG thermograms of PAI 9a.

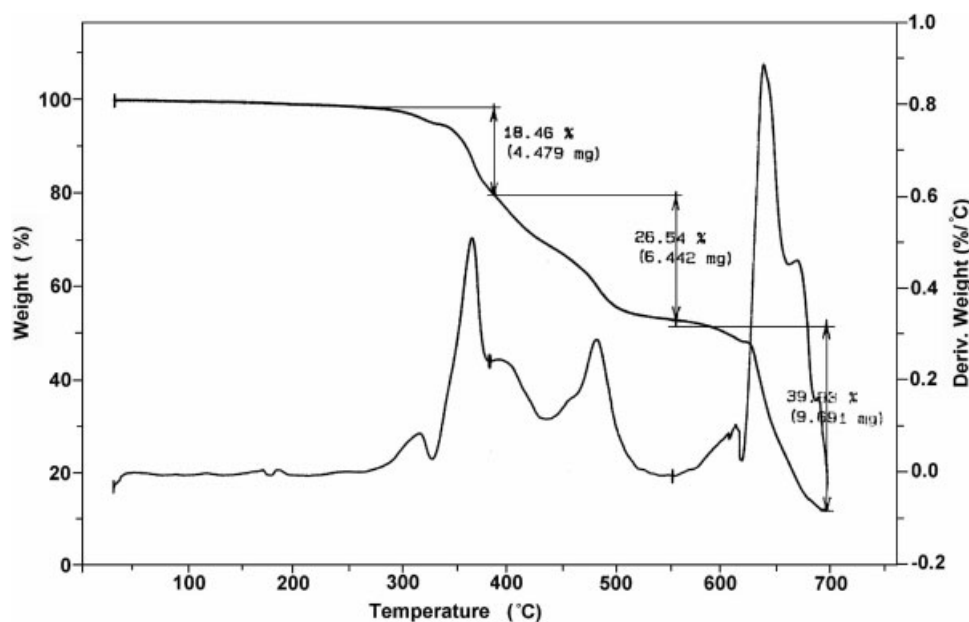


Figure 5 TGA and DTG thermograms of PAI 9b.

polycondensation method and the polymerization reaction of diacid chloride **7** with six different derivatives of hydantoin **8a–f** was performed in DMAc solution in the presence of pyridine as a base. Although we obtained high yield of PAIs **9a–f**, lower inherent viscosities resulted. Therefore, microwave-assisted polycondensation proceeds rapidly and the products have higher inherent viscosities in a shorter period of time in comparison with solution polycondensation. The reaction yields and some physical data of the solution polycondensation are listed in Table II. PAIs **9a–f** derived from monomer **7** show different colors from pale yellow to brown. As shown in Table I, these polymers were obtained in quantitative yields with inherent viscosities between 1.15–1.50 dL/g. The structures of these polymers were confirmed as PAIs by means of FTIR spectroscopy and elemental analyses. The representative FTIR spectrum of PAI **9c** is shown in Figure 3. The polymer exhibited characteristic absorption bands at 1778, 1722 cm^{-1} for the imide ring (asymmetric and symmetric C=O stretching vibrations), 1370 cm^{-1} (C–N stretching vibration), 1160 and 725 cm^{-1} (imide ring deformations).

The elemental analyses of the resulting PAIs **9a–f** were in good agreement with the calculated values for the proposed structures (Table III).

The solubility of PAIs **9a–f** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers are soluble in organic solvents such as DMF, DMAc, DMSO, NMP, and acetone at room temperature, and are insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water. The high solubility of the obtained PAIs was apparently due to the introduction of *m*-phenylene structure and

phosphine oxide linkages, which resulted in increasing free volume between the polymer chains and decreasing intermolecular interactions (Table IV).

Thermal analysis and flame retardant properties

The thermal properties of the PAIs **9a–f** were investigated by means of TGA and DTG analyses under a nitrogen atmosphere at a heating rate of 10°C/min (Figs. 4 and 5).

All polymers showed almost similar decomposition behavior. Initial decomposition temperature, 5 and 10% weight loss temperature (T_5 , T_{10}), and char yields at 600°C are summarized in Table V. These polymers exhibited good resistance to thermal decomposition up to 305–400°C under nitrogen and began to decompose gradually above that temperature. The temperatures of 5% weight loss for all the polymers ranged from 305 to

TABLE V
Thermal Behavior of PAIs 9a–f

Polymer	T_5 (°C) ^a	T_{10} (°C) ^a	Char yield ^b	LOI ^c
9a	340–345	360–365	38	29
9b	350–355	365–370	53	32
9c	380–385	420–425	47	33
9d	305–310	355–360	57	29
9e	400–405	440–445	53	34
9f	320–325	405–410	60	32

^a Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10°C/min under N₂.

^b Weight percentage of material left after TGA analysis at a maximum temperature of 600°C under N₂.

^c LOI, Limited oxygen index.

400°C and the residual weight at 600°C ranged from 38 to 60% under nitrogen. The high char yields of these PAIs at high temperature region are important. It shows that these polymers have good thermal stability. Also the flame retardant property of these polymers was evaluated by measuring their LOI values. They showed LOI data between 29 and 34. Generally, materials exhibiting LOI values greater than 26 would show self-extinguishing behavior³⁹ and were considered to be flame retardant. Therefore high char yields data, along with good LOI values between 29 and 34, indicated that these polymers have good flame retardant properties.

CONCLUSIONS

A new series of PAIs **9a–f** containing phosphine oxide moieties were synthesized by two different methods such as microwave assisted polycondensation and solution polycondensation reactions of an equimolar mixture of monomer **7** with six different derivatives of hydantoin **8a–f**. These polymers showed excellent solubilities and thermal stability. The high char yields and good LOI data of these polymers showed that the introduction of phosphine oxide moieties into the backbone increased the thermal stability and flame-retardant property. These properties can make these polymers attractive for practical applications such as processable high-performance engineering plastics. In addition, the above-mentioned results demonstrate that microwave irradiation is a valuable optimization method, since it dramatically reduces reaction time and increases inherent viscosities of obtained polymers.

APPENDIX: THE POLY(AMIDE-IMIDE)S **9a–f** ANALYSES USING FTIR

Polymer **9a**

FTIR (KBr): 3050 (w), 1776 (w), 1724 (s), 1662 (s), 1590 (w), 1489 (s), 1371 (m), 1224 (s), 1168 (m), 850 (w), 725 (m), 628 (m) cm^{-1} .

Polymer **9b**

FTIR (KBr): 3067 (m), 1778 (w), 1724 (s, br), 1682 (m), 1593 (m), 1511 (s), 1475 (m), 1371 (sm), 1290 (m), 1140 (m), 750 (w) cm^{-1} .

Polymer **9c**

FTIR (KBr): 3059 (w), 1778 (w), 1722 (s), 1660 (s), 1592 (w), 1486 (s), 1370 (m), 1222 (s), 1160 (m), 830 (w), 725 (w), 625 (w) cm^{-1} .

Polymer **9d**

FTIR (KBr): 3067 (w), 1782 (w), 1724 (s, br), 1665 (m), 1591 (m), 1485 (s), 1425 (m), 1373 (s), 1215 (m), 1190 (w), 725 (m) cm^{-1} .

Polymer **9e**

FTIR (KBr): 3061 (w), 1776 (w), 1724 (s), 1662 (s), 1593 (w), 1498 (s), 1371 (m), 1224 (s), 1169 (m), 720 (w), 628 (m) cm^{-1} .

Polymer **9f**

FTIR (KBr): 3014 (w), 1782 (m), 1724 (s), 1682 (m, br), 1591 (s), 1510 (m), 1498 (m), 1371 (m), 1290 (m), 1147 (m), 752 (w) cm^{-1} .

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