

# Synthesis and Characterization of New Flame-Retardant Polyaryl Phosphoramidate Esters Containing Furan and Thiophene Units

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## SYNOPSIS

Two series of new flame-retardant polyaryl phosphoramidate esters were synthesized by low-temperature solution polycondensation from arylphosphorodichlorides with 3,4-bis(4-aminophenyl)2,5-diphenylfuran and 2,5-bis(4-aminophenyl)3,4-diphenylthiophene. The polymers were characterized by IR,  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR spectroscopy and elemental analysis. The thermal stability and flammability were studied by thermogravimetry and limiting oxygen index, respectively. © 1995 John Wiley & Sons, Inc.

## INTRODUCTION

Organophosphorus polymers have gained considerable interest as flame-retardant polymers. The versatility of the phosphorus atom can be utilized to synthesize a wide range of fire-retardant polymers. These phosphorus-containing polymers offer an attractive combination of chemical, physical, and mechanical properties in addition to their flame retardancy. However, rigid aromatic structures possess high melt or glass transition temperatures and also limited solubility in organic solvents. They are detrimental in processing the polymers. Incorporation of flexible pendent phenyl groups into the polymer backbone is an effective method of enhancing the solubility without sacrificing their inherent thermal stability. Functional groups bearing tetraphenyl thiophene and tetraphenyl furan monomers are suitable candidates to impart such properties.<sup>1,2</sup> Literature on polyphosphoramidate esters are scarce. Continuing our research on the application of polyphosphate esters<sup>3-9</sup> as a flame-retardant polymeric additives, we report here a new series of polyaryl-phosphoramidate esters. The present work deals

with the synthesis and characterization of polyphosphoramidate esters derived from 3,4-bis(4-aminophenyl)2,5-diphenylfuran and 2,5-bis(4-aminophenyl)3,4-diphenylthiophene with different arylphosphorodichlorides via a low-temperature solution polycondensation method.

## EXPERIMENTAL

### Material

Phosphorus oxychloride (Fluka), benzyl chloride (Ranbaxy), acetic acid (Ranbaxy), and tetrahydrofuran (THF) (Ranbaxy) were purified by distillation. Stannous chloride (Sigma) and phenylacetic acid (Aldrich) were used as received.

### Arylphosphorodichlorides (APC)

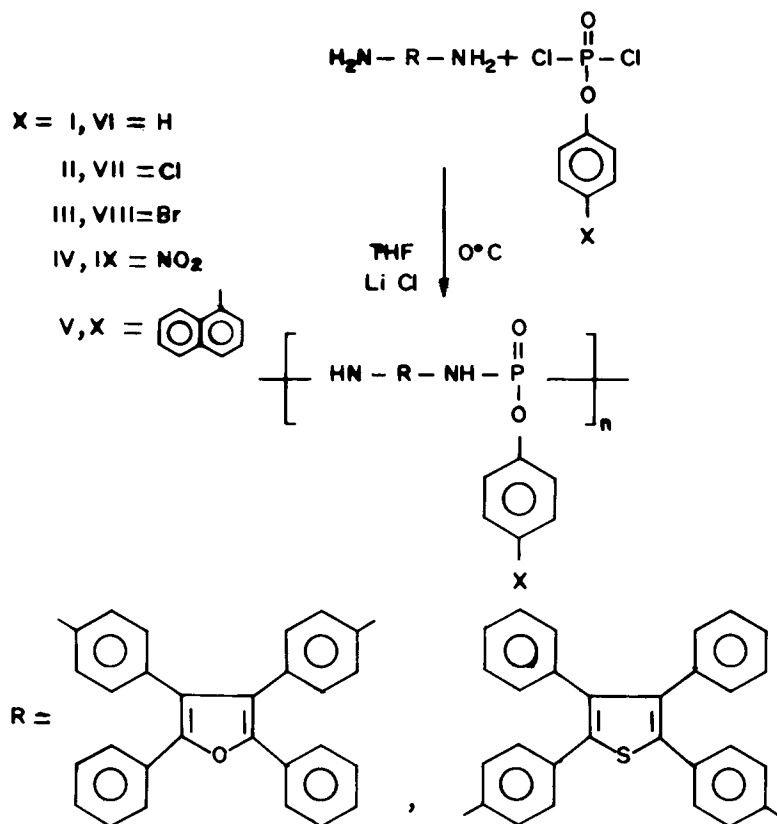
The different APCs [ $\text{X-C}_6\text{H}_4\text{OP(O)Cl}_2$ ; X = H, Cl, Br,  $\text{NO}_2$  and -naphthyl, respectively] were prepared from  $\text{POCl}_3$  and corresponding phenols and naphthol in the presence of catalytic amount of anhydrous aluminum chloride as reported elsewhere.<sup>10</sup>

### 3,4-bis(4-aminophenyl)2,5-diphenylfuran (APDF)

Deoxybenzoin was obtained from the reaction of phenylacetic acid,  $\text{POCl}_3$ , and benzene by the reported procedure.<sup>11</sup> They were subsequently converted into 4-nitrodeoxybenzoin by reacting it with

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Scheme I Synthesis of polyarylphosphoramidate esters (I-X).

cupric nitrate in acetic anhydride.<sup>12</sup> Further reaction of 4-nitrodeoxybenzoin with sodium ethoxide in the presence of iodine yielded 1,2-bis(4-nitrophenyl)-1,2-dibenzoylthane, which was then cyclodehydrated by treating with dry HCl gas in acetic acid to give 3,4-bis(4-nitrophenyl)2,5-diphenylfuran, which was finally reduced by stannous chloride to give the title compound.<sup>2</sup>

#### 2,5-bis(4-aminophenyl)3,4-diphenylthiophene (APDT)

2,5-bis(4-aminophenyl)3,4-diphenylthiophene was prepared from benzyl chloride and sulfur in three steps according to the procedure reported by Imai et al.<sup>1</sup>

#### Polymerization

The polyphosphoramidate esters were prepared by low-temperature solution polycondensation, a typical procedure for the synthesis of polymer I (Scheme I) is as follows. To a 20-mL solution of 5% LiCl in THF, APDF (1 mmol) was dissolved at low temperatures (0–10°C) under nitrogen atmosphere.

Subsequently, 20 mL dry THF solution of phenylphosphorodichloride (1.1 mmol) was added dropwise over a period of 30 min with vigorous stirring. The mixture was stirred at that temperature for 1 h and then gradually allowed to cool at room temperature. The reaction was continued for a further 12 h. At the end of the reaction period the viscous solution was poured into excess water. The precipitated product was filtered, washed with water, acetone, and methanol followed by drying *in vacuo* at 70°C for 12 h. The remaining polymers APC-APDF (II-V) and APC-APDT (VI-X) were prepared in a similar manner. The polymer yield was 65–75%. All the polymers were brown in color and powdery. They are soluble in DMF, DMAc, and NMP but insoluble in common organic solvents such as chloroform and acetone.

#### Characterization

The elemental analysis was performed on a Heraeus CHNO rapid analyzer. The infrared (IR) spectra of the polymers were recorded in KBr pellets on a Perkin-Elmer Model 715 spectrophotometer. The <sup>1</sup>H and <sup>13</sup>C NMR spectra were obtained in DMSO-d<sub>6</sub>

Table I Elemental Analysis of the Polymer

Polymer	Elemental Analysis					
	C		H		N	
	Calc.	Found	Calc.	Found	Calc.	Found
I	75.54	75.15	4.66	4.82	5.17	5.06
II	71.02	70.76	4.20	4.12	4.86	4.91
III	65.92	64.82	3.90	4.00	4.52	4.49
IV	69.74	68.17	4.13	4.20	7.17	7.07
V	77.27	76.20	4.60	4.55	4.74	4.38
VI	73.37	72.06	4.52	4.53	5.03	4.88
VII	69.09	66.57	4.09	4.32	4.73	4.93
VIII	64.36	62.11	3.81	3.78	4.41	4.35
IX	67.88	64.18	4.02	3.98	6.98	6.41
X	75.23	73.89	4.48	4.14	4.61	4.42

using TMS as internal standard on a Bruker FT200 and Bruker FT270 spectrometer, respectively.  $^{31}\text{P}$  NMR spectra were recorded on a Varian FT80A spectrometer in  $\text{DMSO-d}_6$  under broadband  $^1\text{H}$  decoupling conditions.  $\text{D}_2\text{O}$  and phosphoric acid (85%) were used as external lock and external standard, respectively.

#### Thermal and Flammability Studies

The thermogravimetry (TG) studies were carried out on Shimadzu DT40 and Mettler TA2000 thermal analyzers, in nitrogen, at a heating rate of  $20^\circ\text{C min}^{-1}$  with a sample of 3–5 mg. The limiting oxygen

index (LOI) data were obtained on an apparatus fabricated in accordance with the ASTM-D2863-70 standard; the measurements were made using a modified procedure.<sup>13</sup>

#### RESULTS AND DISCUSSION

Two series of polyarylphosphoramidate esters containing furan and thiophene units were prepared by the solution polycondensation method (Scheme I). In the present study, though low-temperature solution polymerization has been employed, no acid acceptors were used. This is because arylphospho-

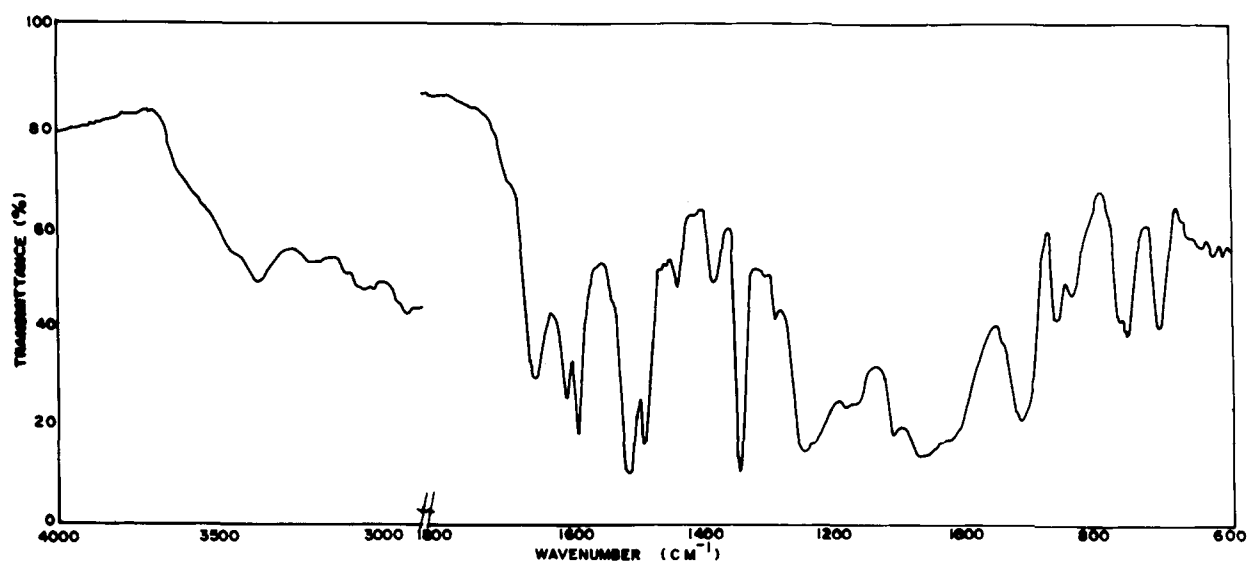


Figure 1 Infrared spectrum of polymer IX.

rodichlorides react with pyridine to form a complex. Similarly, the aprotic solvents also react in the same monomer. For this reason, dry THF has been employed as a solvent. LiCl was used to improve the polarity of the solvent; in its absence the product precipitated within 30 min. All the polymers were prepared by keeping the diamine-to-dichloride ratio 1 : 1.1 so that the polymer end groups are comprised mainly of the phosphorus units.

The molar masses of the polymers were confirmed by elemental analysis; the results are shown in Table I. The IR spectrum of polymer IX is shown in Figure 1. The absorption bands near 3280 and 1300  $\text{cm}^{-1}$  correspond to  $\text{—NH—}$  and  $\text{P=O}$  stretching, respectively. All the polymers showed absorption around 1320, 1180, and 960  $\text{cm}^{-1}$  owing to the  $\text{P—N—C}$  (aromatic) and  $\text{P—O—C}$  (aromatic) stretchings.<sup>14,15</sup> The other absorption bands correspond to aromatic or functional groups present in the polymer, such as, for example, 3060  $\text{cm}^{-1}$  (aromatic  $\text{C—H}$ ) and 1595  $\text{cm}^{-1}$  (aromatic  $\text{C=C}$ ), which support the formation of polyphosphoramidate esters.

A representative  $^1\text{H}$  NMR spectrum of polymer IV is shown in Figure 2. The aromatic protons resonate in the 6.7–8.2  $\delta$  region due to high aromaticity of the polymer backbone; the proton signals intermixed and appeared as a broad multiplet. The  $\text{—NH—}$  proton appeared in the 5.5  $\delta$  region and disappeared in some polymer spectra due to the high degree of polymerization.

A typical broadband  $^1\text{H}$  decoupled  $^{13}\text{C}$  NMR spectrum of polymer IX is shown in Figure 3. All the aromatic carbons including thiophene carbons

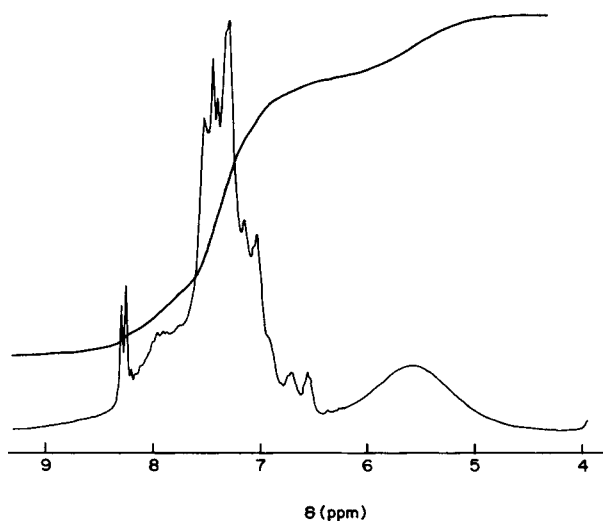


Figure 2  $^1\text{H}$  NMR spectrum of polymer IV.

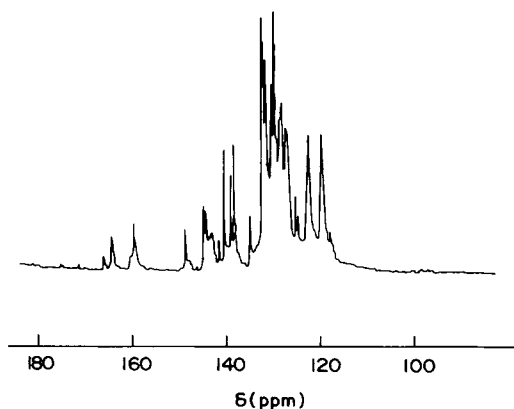
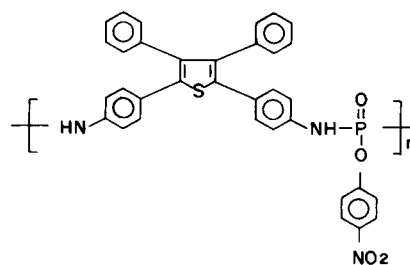


Figure 3 Broadband decoupled  $^{13}\text{C}$  NMR spectrum of polymer IX.

resonate in the 120–162  $\delta$  region. Because of the high aromaticity, the carbon resonances overlap and appear as a broad multiplet in the 126–136  $\delta$  region.

The representative  $^{31}\text{P}$  NMR spectrum of polymer X is shown in Figure 4. The negative chemical shifts were observed in the  $-7.2$   $\delta$  and  $-12.69$   $\delta$  region. The splitting of the phosphorus resonances in the  $-7.2$   $\delta$  region, by hydrogen of the  $\text{P—N—H}$  bond,

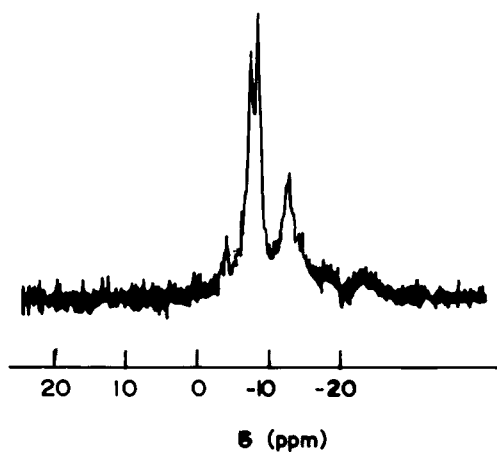


Figure 4  $^{31}\text{P}$  NMR spectrum of polymer X.

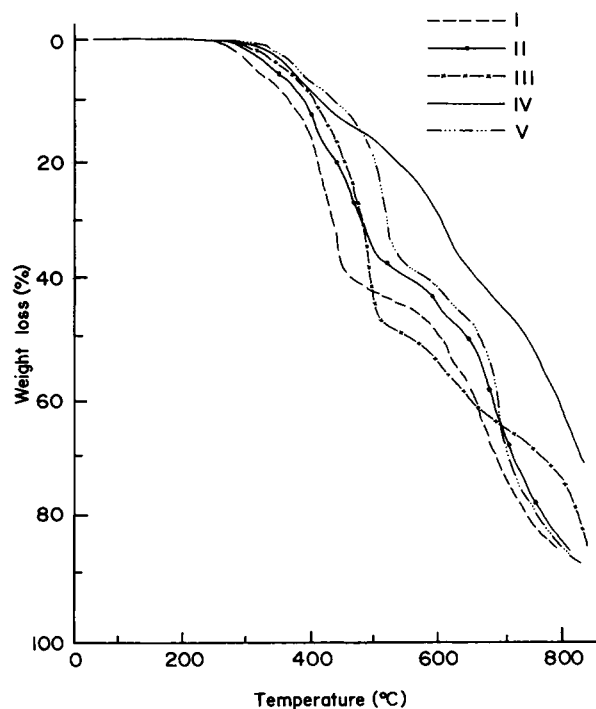


Figure 5 TG traces of polymers I-V.

probably indicate the covalent character in the bond. Splitting may also arise on account of electrical quadrupole moment of the interconnection nitrogen nucleus.<sup>16</sup> The resonance at  $-12 \delta$  may be attributed to the phosphorus end group as  $P-O-H$ .<sup>17</sup>

The thermal stability of the polymers was evaluated by thermogravimetric analysis in nitrogen atmosphere. Figures 5 and 6 show the typical TG traces of the polymers. The initial (1%) decomposition, 50% weight loss, and char % at 700°C are summarized in Table II. In general, these polymers are stable up to 250–350°C in nitrogen atmosphere and start degrading thereafter. A two-step degradation pattern is observed in all the cases. The first step corresponds to the formation of various small fragments which subsequently get carbonized in the second step. The unsubstituted pendent phenyl polymer exhibited a significantly lower thermal stability than others. In both series (APC-APDF and APC-APDT) the higher thermal stability of polymers II-IV and VI-IX is due to their substitution. The nitro and chloro substitutions offer a higher char yields. The pendent naphthyl polymers give higher char yields compared to other polymers. The polymers derived from APC-APDT (VI-X) show an improved thermal stability and have an edge in terms of the char percentages, as compared to the polymers derived from APC-APDF (I-V). This may

be attributed to the thiophene unit, which is more stable compared to the furan structure. The char yield at 700°C varied from 35 to 65 for these polymers, depending on the backbone structures.

Flame retardancy of these polymers was compared from their LOI values (Table II). The present class of polymers are distinguished by their low flammability as demonstrated by high LOI values. The flammability of the polymers depends on their substituents too. The *p*-NO<sub>2</sub> polymers of both series have significantly higher LOI values than others. In the case of halogen substitution the *p*-bromo polymers were slightly better than the *p*-chloro polymer. The LOI value for the pendent naphthyl polymer shows a higher LOI, which may be ascribed to their higher aromaticity. Here again, the thiophene-unit-containing polymers (APC-APDT, VI-X) showed better flame retardancy than the furan-containing polymers (APC-APDF, I-V).

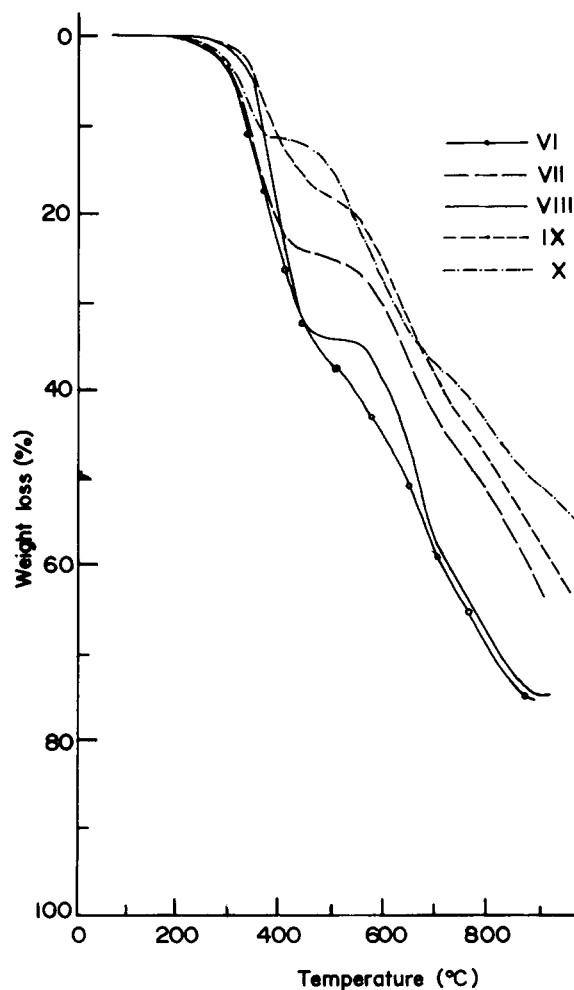


Figure 6 TG traces of polymers VI-X.

**Table II Thermal and Flammability Data of Polymers**

Polymer	Temperature (°C) Corresponds to		Char at 700°C <sup>a</sup>	LOI <sup>b</sup> %
	1% Weight Loss	50% Weight Loss		
I	252	602	26	32
II	264	634	33	33
III	324	575	38	36
IV	330	751	54	41
V	335	660	30	45
VI	270	640	42	38
VII	282	780	59	38
VIII	320	680	48	41
IX	350	800	60	45
X	290	880	65	49

<sup>a</sup> Estimated error  $\pm 1\%$ .<sup>b</sup> Estimated error  $\pm 2\%$ .

## CONCLUSION

Two series of phosphoramidate esters have been synthesized from 3,4-bis(4-aminophenyl)2,5-diphenylfuran and 2,5-bis(4-aminophenyl)3,4-diphenylthiophene with arylphosphorodichlorides by low-temperature polycondensation, which were characterized spectroscopically. These polymers exhibit higher thermal stability as well as low flammability. The thermal stabilities of these polymers were found to strongly depend on their substitution; introduction of naphthyl unit in the side chain was found to substantially reduce the flammability. Finally, it may be concluded that the thiophene-unit-containing polymers exhibit superior thermal and flame resistance behavior compared to that of furan-containing polymers.

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