

A New Flame-Retardant Polyamide Containing Phosphine Oxide and N,N-(4,4-diphenylether) Moieties in the Main Chain: Synthesis and Characterization

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A new flame-retardant polyamide containing phosphine oxide moieties in the main chain was synthesized from the solution polycondensation reaction of bis(3-aminophenyl) phenyl phosphine oxide with N,N-(4,4-diphenylether) bis trimellitimide, using thionyl chloride, N-methyl-2-pyrrolidone, and pyridine as condensing agents. This new polymer was obtained in high yield (92%), has high inherent viscosity (0.73 dL/g), and was characterized by elemental analysis, FT-IR spectroscopy, thermal gravimetric analysis (TGA and DTG), and solubility testing. Furthermore, another polyamide was prepared by the solution polycondensation reaction of N,N-(4,4-diphenylether) bis trimellitimide with 1,4-phenylene diamine, and its flame-retardant behavior was compared to that of the previous one.

Key Words: Flame-retardant polymers, phosphine oxide moieties, N,N-(4,4-Diphenylether) bis trimellitimide.

Introduction

Over the course of recent decades, conventional materials, such as metals, wood, glass, and ceramic, have been increasingly replaced by synthetic polymers, due to their versatility, low density, good mechanical and physical properties, and the ease with which they can be molded.^{1,2} However, these advantages of polymeric materials are shadowed by their flammability and low stability in high temperatures in comparison to metals. In recent years, considerable attention has been focused on preparing flame-retardant polymers,^{3,4} 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).¹⁰⁻¹⁷ Among the polymers with phosphorus moieties, 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.¹⁷⁻²³

In this article, a new flame-retardant polyamide (**8**) containing phosphine oxide and N,N-(4,4-diphenylether) moieties in the main chain was prepared by the solution polycondensation reaction of bis(3-aminophenyl) phenyl phosphine oxide (**4**) (as a diamine with phosphine oxide moiety), with N,N-(4,4-diphenylether) bis trimellitimide (**7**), using thionyl chloride, N-methyl-2-pyrrolidone, and pyridine as condensing agents. Furthermore, the flame-retardant property of this new polyamide (**8**) was compared to that of a polyamide (**10**) prepared by the solution polycondensation reaction of N,N-(4,4-diphenylether) bis trimellitimide (**7**) with 1,4-phenylene diamine (**9**) by TGA, DTG, and LOI techniques, and the results showed that the incorporation of phosphine oxide moieties in the main chain dramatically increased the flame-retardant property in this polymer. This new polyamide is brown, is soluble in various organic solvents, and has good thermal stability. These properties could make this polymer attractive for practical applications, such as processable high-performance engineering plastics.

Experimental

Materials

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

Techniques

¹H-NMR spectra (400 MHz) were recorded on a Bruker Advanced 400 (Germany). Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectral analyses of solids were performed using KBr pellets. Vibrational transition frequencies are reported in wave number (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®Viscometer. Thermal gravimetric analysis (TGA and DTG) data for polymers were performed on a Mettler TA4000 system under N₂ atmosphere at a rate of 10 °C/min. Differential scanning calorimetries (DSC) were recorded on a Stanton Redcraft STA-780 with a heating rate of 10 °C/min in air. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran. Limited oxygen indexes (LOI) were measured on a Stanton Redcraft flame meter.

Monomer synthesis

Bis (3-aminophenyl) phenyl phosphine oxide (**4**)

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

Triphenyl phosphine oxide (**2**)

Into a 100 mL round-bottomed flask were placed 4.94 g (20 mmol) of triphenyl phosphine (**1**), 12 mL of absolute ethanol, 20 mL of tetrachloromethane, and a stirring bar. The mixture was refluxed for 4 h. The solvent was removed under reduced pressure and the residue was added to 100 mL of cold water. A white crystalline substance was formed; then the precipitate was filtered off and dried to give 4.24 g (81%) of

compound **2**: mp 154-157 °C, FT-IR (KBr): 3074 (m), 3038 (m), 1774 (m), 1589 (m), 1483 (m), 1437 (s), 1180 (s), 1118 (s, br), 997 (w), 854 (w), 721 (s, br), 797 (s) cm⁻¹.

Bis (3-nitrophenyl) phenyl phosphine oxide (3)

Into a 250 mL round-bottomed flask equipped with a stirrer were placed 2.78 g (100 mmol) of triphenyl phosphine oxide² and a mixture of 200 mL of 97% sulfuric acid. The reactant was dissolved and the reaction system was then cooled to -5 °C with an ice/salt bath. Then 14.5 g (230 mmol) of a solution of fuming nitric acid in 100 mL of sulfuric was added dropwise over 2 h, and the reaction system was maintained at room temperature for an additional 8 h. The reaction solution was then hydrolyzed over 2 L of ice. After the ice melted, the mixture was extracted with chloroform and washed with sodium bicarbonate aqueous solution until the neutral pH and the solvent were removed. Finally, the solid residue was recrystallized with absolute ethanol and then 25.70 g (70%) of bis(3-nitrophenyl) phenyl phosphine oxide (**3**) yellow crystals was obtained: mp 245-248 °C, FT-IR (KBr): 3082 (m), 2924 (w), 2882 (w), 1774 (w), 1708 (w), 1523 (s), 1477 (w), 1347 (s), 1278 (m), 1197 (s), 1140 (m), 1095 (m), 881 (m), 731 (m), 775 (s) cm⁻¹. Analysis: Calculated for C₁₈H₁₃N₂OP: C, 58.71; H, 3.53; N, 7.60; found: C, 58.60; H, 3.70; N, 7.50.

Bis (3-aminophenyl) phenyl phosphine oxide (4)

We added 15.4 g (50 mmol) of bis(3-nitrophenyl) phenyl phosphine oxide (**3**) into a 500 mL round-bottomed flask containing 144 g of powdered tin(II) chloride dihydrate, to which a solution of 170 mL of fuming hydrochloric acid in 320 mL of ethanol was added. The reaction mixture was stirred at room temperature for 5 h, after which time the solution was concentrated and then neutralized by a 25% NaOH aqueous 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 9.41 g (73%) of bis(3-aminophenyl) phenyl phosphine oxide (**4**) yellow crystals was obtained: mp 115-117 °C, FT-IR (KBr): 3325 (m), 3200 (m), 3070 (w), 1730 (m), 1593 (s), 1483 (m), 1437 (s), 1313 (m), 1277 (w), 1175 (s), 830 (w), 729 (m), 705 (s), 503 (m) cm⁻¹, ¹H NMR (400 MHz, DMSO-d₆, TMS): δ 5.30-5.40 (br, 4H); 6.55-6.60 (m, 2H); 6.65-6.70 (d, 2H); 6.70-6.75 (d, 2H); 7.10-7.15 (m, 2H), 7.45-7.55 (br, 5H) ppm. Analysis: Calculated for C₁₈H₁₇N₂OP: C, 70.14; H, 5.51; N, 9.08; found: C, 70.71; H, 5.74; N, 8.91.

N,N-(4,4-diphenylether) bistrimellitimide (7)

This compound was prepared according to a typical procedure, shown in Scheme 2.²³

N,N-(4,4-diphenylether) bistrimellitimide (7)

Into a 250 mL round-bottomed flask were added 3.84 g (20 mmol) of trimellitic dianhydride (**5**), 2.00 g (10 mmol) of 4,4-diaminodiphenyl ether (**6**), 80 mL of a mixture of acetic acid and pyridine (3:2), and a stirring bar. The mixture was stirred at room temperature overnight and then 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 yellow precipitate was formed and the precipitate was filtered off and dried to give 4.95 g (90.3%) of the yellow crystal compound **7**: mp 392-394 °C, FT-IR (KBr): 3500-2800 (m, br), 1780 (w, sh), 1730-1700 (s, br), 1708 (m), 1507(s), 1425 (w), 1392 (s),

1307 (s), 1300 (m), 1257-1200 (s, br), 1178 (m), 1118 (m), 1100 (m), 927 (w), 883 (w), 827 (m), 727 (m) cm^{-1} . Analysis: Calculated for $\text{C}_{30}\text{H}_{17}\text{N}_2\text{O}_9$: C, 75.71; H, 2.92; N, 5.10; found: C, 75.50; H, 3.10; N, 4.80.

Polymer Synthesis

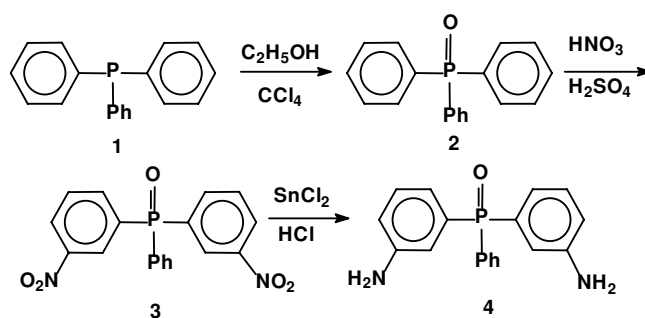
The polyamide **8** was prepared by the following procedure: 1 mmol of N,N-(4,4-diphenylether) bistrimellitamide (**7**) was dissolved in 5 mL of N-methyl pyrrolidone in a dry 3-necked flask. The solution was cooled to $-10\text{ }^\circ\text{C}$ and 0.298 g (2.5 mmol) thionyl chloride was added, followed by stirring for 2 min. Then 1 mmol of diamine (**4**) and pyridine (0.198 g, 2.5 mmol) were added to the mixture. It was stirred for 15 h at $0\text{ }^\circ\text{C}$ and then for 2 h at room temperature. The viscous reaction mixture was added to 25 mL of methanol. The precipitated polymer (**8**) was collected by filtration and was dried at $80\text{ }^\circ\text{C}$ for 8 h under vacuum, leaving a brown solid.

Furthermore, the polyamide **10** was also prepared by the above procedure.

Results and Discussion

Monomer synthesis

Bis(3-aminophenyl) phenyl phosphine oxide (**4**) was prepared in 3 steps from a simple organic compound, such as triphenyl phosphine (**1**), as shown in Scheme 1. At first, triphenyl phosphine (**1**) was oxidized to triphenyl phosphine oxide (**2**); then this compound was converted to bis(3-nitrophenyl) phenyl phosphine oxide (**3**) by using concentrated nitric acid in the presence of sulfuric acid. Bis(3-nitrophenyl) phenyl phosphine oxide (**3**) was reduced to bis(3-aminophenyl) phenyl phosphine oxide (**4**) with SnCl_2 .



Scheme 1.

The chemical composition and purity of phosphorus containing diamine (**4**) were analyzed by $^1\text{H-NMR}$ and FT-IR spectroscopy, melting point, and elemental analysis. The elemental analysis closely corresponded to the calculated ones, demonstrating that the expected compounds were obtained. Figure 1 displays the FT-IR spectrum of bis(3-aminophenyl) phenyl phosphine oxide (**4**). Peaks appearing at 3325 and 3200 cm^{-1} indicated the existence of amine groups (N-H stretching vibration). Other peaks at 1165 (P=O) and 1437 cm^{-1} (P-Ph) confirmed the presence of phosphine oxide moiety in this compound.

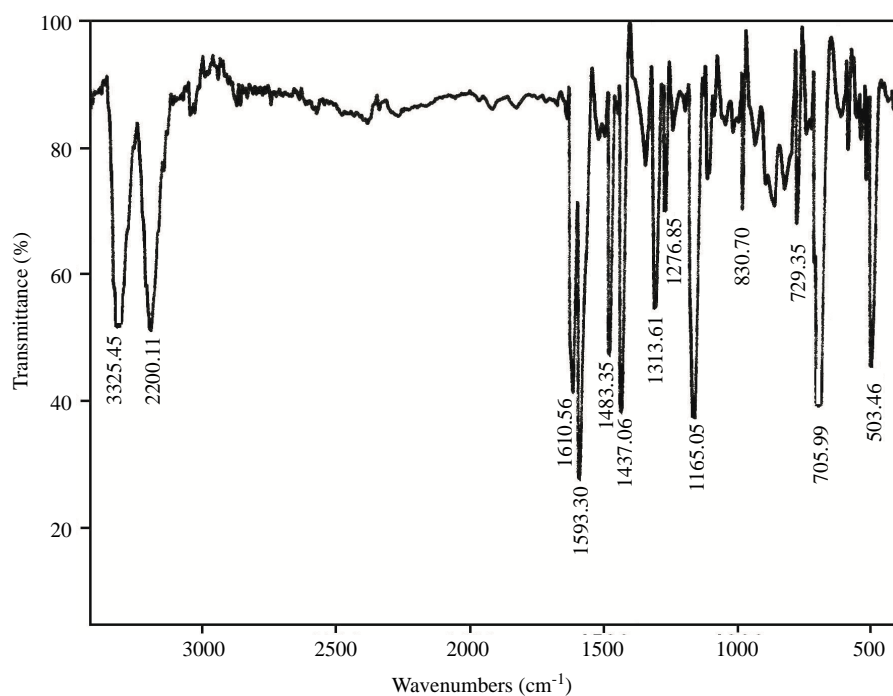


Figure 1. FT-IR Spectrum of diamine 4.

Figure 2 shows the $^1\text{H-NMR}$ spectrum of bis (3-aminophenyl) phenyl phosphine oxide (4). Peaks appearing at 5.4 ppm indicated the existence of amine groups (NH_2). Other peaks appearing at 6.6-7.6 ppm show 2 different aromatic rings in this compound.

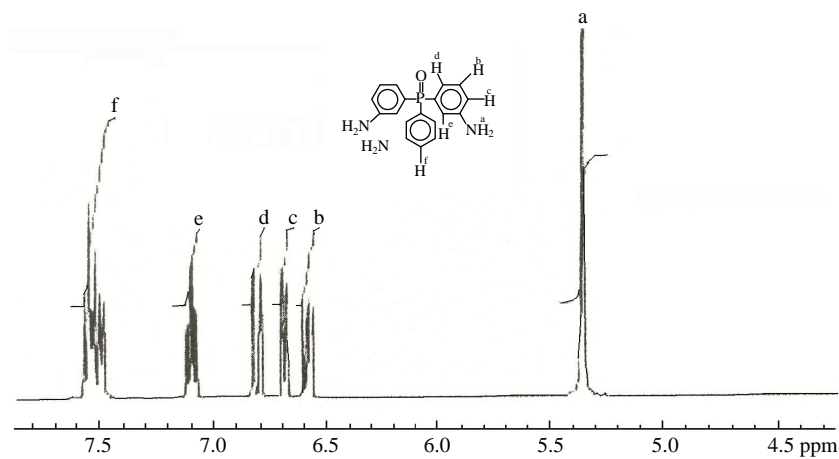
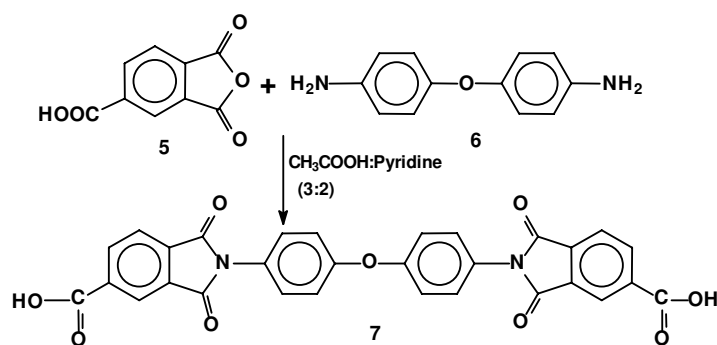


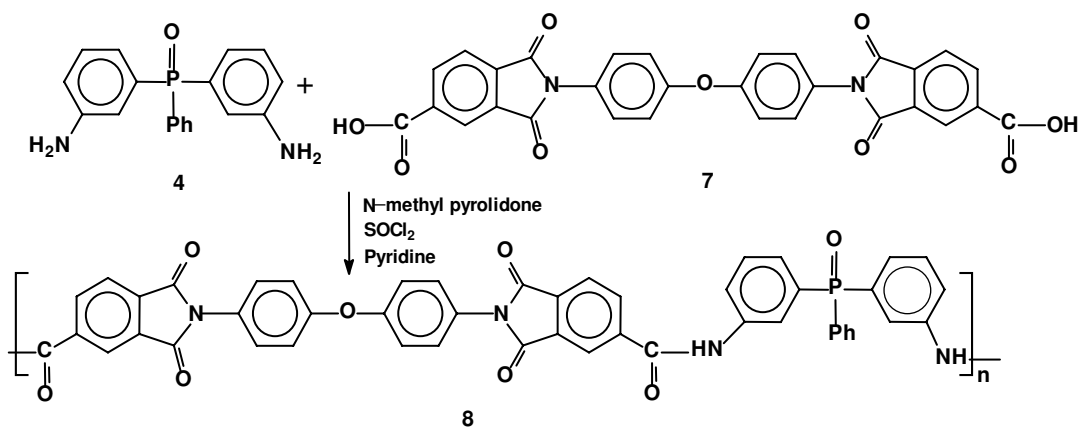
Figure 2. $^1\text{H-NMR}$ Spectrum of diamine 4 (400 MHz).

N,N-(4,4-diphenylether) bis trimellitimide (7) was prepared from the condensation reaction of 2 equimolar trimellitic anhydrides (5) with 4,4-diaminodiphenyl ether (6) in a mixture of acetic acid and pyridine as solvent (Scheme 2). Moreover, the chemical composition and purity of diimide acid (7) was analyzed by FT-IR spectroscopy, melting point, and elemental analysis. In the FT-IR spectrum, a broad peak at $2800\text{-}3500\text{ cm}^{-1}$ confirmed the presence of an OH group in this compound. Absorption bands at 1780 and 1724 cm^{-1} are related to carbonyl groups of acid and an imide ring. Furthermore, absorption bands in 1390 and 750 cm^{-1} (imide characteristic ring vibration) confirmed the presence of an imide ring.

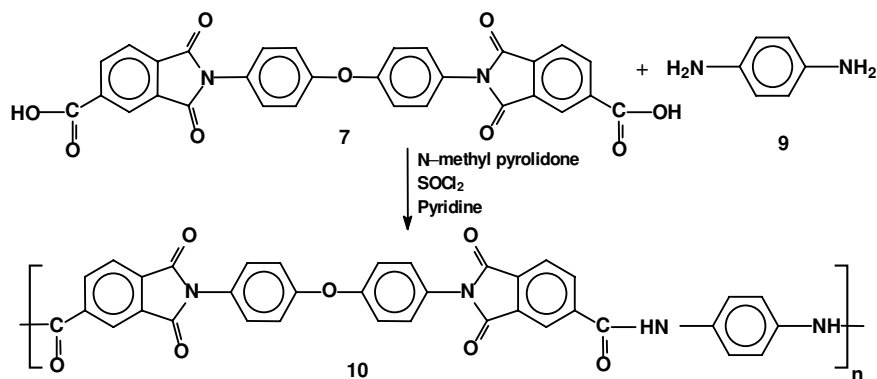


Polymer synthesis

The polyamide **8** was synthesized by the polycondensation reaction of bis (3-aminophenyl) phenyl phosphine oxide (**4**) with N,N-(4,4-diphenylether) bis trimellitimide (**7**) (Scheme 3), using thionyl chloride, N-methyl-2-pyrrolidone, and pyridine as condensing agents.



The flame-retardant property of polyamide (**8**) was compared to that of another polyamide (**10**) without phosphine oxide moiety, which was synthesized by direct the polycondensation reaction of N,N-(4,4-diphenylether) bis trimellitimide (**7**) with 1,4-phenylene diamine (**9**) (Scheme 4) by the same procedure.



The polyamide **8** has inherent viscosity of 0.73 dL/g. The structure of this polymer was confirmed as polyamide by means of FT-IR spectroscopy and elemental analysis. The representative FT-IR spectrum of this compound is shown in Figure 3. The polymer shows absorption bands between 3300 and 3400 cm^{-1} due to an N-H amide group. Absorption bands at 1778 and 1722 cm^{-1} are related to carbonyl groups of acid and an imide ring. Absorption bands around 1240 cm^{-1} (P=O) and 1500 cm^{-1} (P-Ph) correspond to phosphine oxide moieties in the main chain. The elemental analysis values of the resulting polymers were in good agreement with the calculated values for the proposed structures.

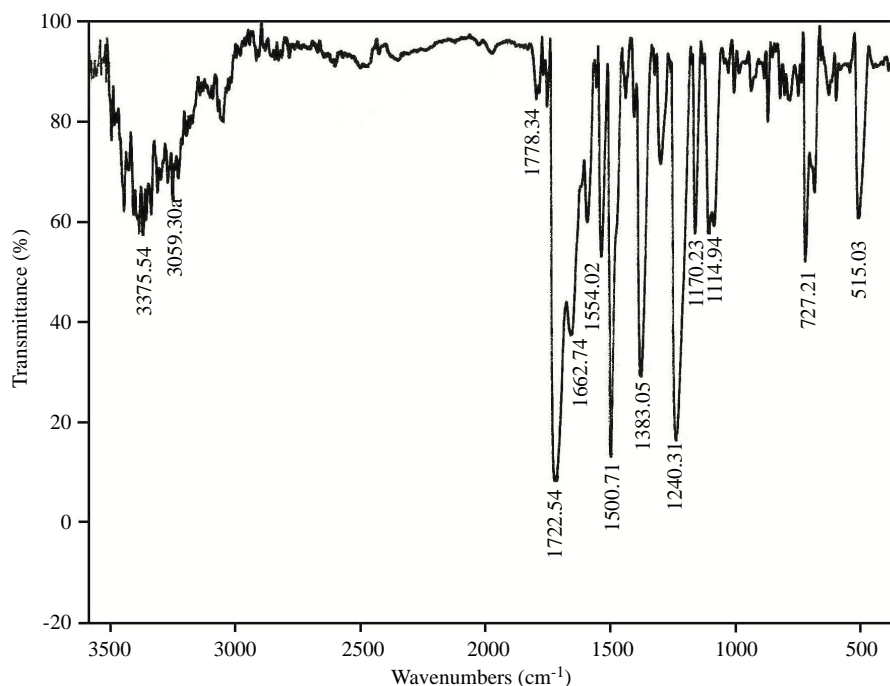


Figure 3. FT-IR Spectrum of polyamide 8.

The solubility of polyamide **8** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. This polymer is soluble in organic solvents, such as dimethyl acetamide, dimethyl sulfoxide, dimethyl formamide, and *n*-methyl pyrrolidone, and is insoluble in solvents, such as chloroform, tetrahydrofurane, acetone, methylene chloride, methanol, ethanol, and water.

The thermal properties of polymers **8** and **10** were investigated by means of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a rate of heating of 10 $^{\circ}\text{C}/\text{min}$ (Table 1). Initial decomposition temperature, 5% and 10% weight loss (T_5 , T_{10}), and char yields at 600 $^{\circ}\text{C}$ for these samples are summarized in Table 1.

Polyamide **8** exhibited good resistance to thermal decomposition up to 340-345 $^{\circ}\text{C}$ in nitrogen and began to decompose gradually above that temperature. The char yield for this polymer at 600 $^{\circ}\text{C}$ is 69% in nitrogen (Figure 4).

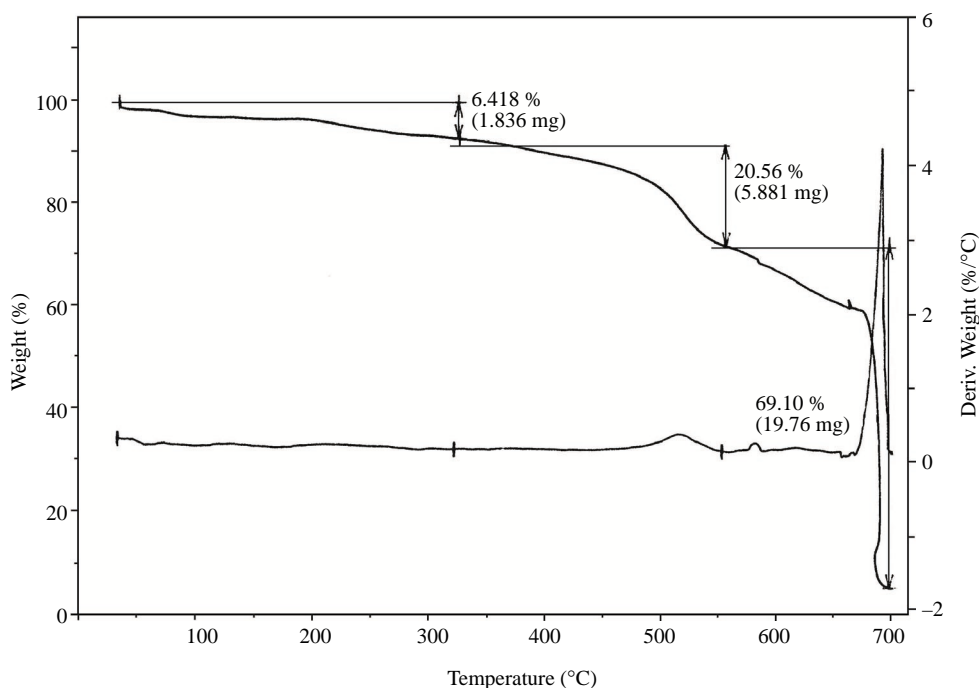


Figure 4. TGA & DTG thermogram polyamide 8.

Table 1. Thermal behavior of polyamides **8** and **10**.

Polymer	T ₅ (°C) ^a	T ₁₀ (°C) ^b	Char Yield ^c	LOI ^d
8	340-345	420-425	69%	29
10	270-275	295-300	41%	21

^{a,b}Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in N₂. ^cWeight percentage of material left after TGA analysis at maximum temperature 600 °C in N₂. ^dLimited oxygen index.

In addition, the flame-retardant property of these polymers was evaluated by measuring their LOI values (Table 1). Polyamide **8** showed good LOI data. Generally, materials exhibiting LOI values > 26 would show self-extinguishing behavior²⁴ and are considered to be flame-retardant; therefore, high char yield data, along with good LOI value of polyamide **10**, indicated that this polymer has good flame-retardant properties. The high LOI data and high char yield showed that the introduction of phosphine oxide moieties in the main chain gives polyamide **8** flame-retardancy.

Conclusion

A new polyamide (**8**) containing phosphine oxide moiety in the main chain was synthesized by the solution polycondensation reaction of an equimolar mixture of bis (3-aminophenyl) phenyl phosphine oxide (**4**) with N,N-(4,4-diphenylether) bis trimellitimide (**7**). This polymer showed good solubility and thermal stability demonstrated by TGA and DTG. The introduction of phosphine oxide moiety into the backbone of the polymer increased flame-retardancy. These properties could make this polymer attractive for such practical applications as processable high-performance engineering plastics.

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