

New Aromatic Polyamide with Azo and Phosphine Oxide Groups in the Main Chain

Khalil FAGHIHI*, Mohsen HAGIBEYGI

*Organic Polymer Chemistry Research Laboratory, Department of Chemistry, Faculty of Science,
Arak University, 38157, Arak-IRAN
e-mail: k-faghihi@araku.ac.ir*

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A new flame-retardant polyamide containing phosphine oxide and azobenzene moieties in the main chain was synthesized by the solution polycondensation reaction of 4,4'-azodibenzoic acid with bis(3-aminophenyl) phenyl phosphine oxide using thionyl chloride, N-methyl-2-pyrrolidone and pyridine. This new polymer was obtained in high yield (96%) and showed high inherent viscosity (0.55 dL/g) and was characterized by elemental analysis, FT-IR spectroscopy, thermal gravimetric analysis (TGA and DTG) and solubility test. Furthermore, another polyamide was prepared by solution polycondensation reaction of 4,4'-azodibenzoic acid with 1,4-phenylene diamine and its flame-retardant behavior was compared by the use of the LOI with the previous one.

Key Words: Flame-retardant polymers, phosphine oxide moieties, 4,4'-azodibenzoic acid.

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. Over the last few years, considerable attention has been paid to the preparation of 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 retardance, high thermal oxidative stability, enhanced solubility in organic solvents, improved miscibility and good adhesion to other compounds.¹⁷⁻²²

Azo-containing polymers are macromolecules with azo groups in the main chain or side chain. Polymers with azobenzene moiety have good stability and usually show high glass transition temperature (T_g).

*Corresponding author

Introducing azobenzene linkages in the polymeric main chain can improve thermal stability and allow broad application as an engineering plastic.^{23,24}

In the present study, a new flame-retardant polyamide (**7**) containing phosphine oxide and azobenzene 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 4,4'-azodibenzoic acid (**6**) by the use of thionyl chloride, N-methyl-2-pyrrolidone and pyridine. Furthermore, the flame retardance of this new polyamide (**7**) was compared with that of a polyamide (**9**) prepared by solution polycondensation reaction of 4,4'-azodibenzoic acid (**6**) with 1,4-phenylene diamine (**8**) by TGA, DTG and LOI, and the results showed that incorporation of phosphine oxide and azobenzene moieties in the main chain dramatically increased the flame retardant property of this polymer. This new polyamide was red, it had good thermal stability and was soluble in various organic solvents. These properties can 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

The ¹H-NMR spectrum (400 MHz) was recorded on a Bruker Avance 400 spectrometer (Germany). The ¹H-NMR spectrum (90 MHz) was recorded on a Varian EM-390. Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrophotometer (England). Spectra of solids were obtained using KBr pellets. Vibrational transition frequencies were reported in wave number (cm⁻¹). Band intensities were 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 recorded on a Mettler TA4000 System under N₂ atmosphere at a rate of 10 °C/min. Differential scanning calorimetry (DSC) was 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. Limiting oxygen index (LOI) were measured on a Stanton Redcraft flame meter.

Monomer synthesis

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

This compound was prepared according to a typical procedure, shown in Scheme 1.²⁵

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; then the solvent was removed under reduced pressure and the residue added to 100 mL of cold water. When

white crystalline was formed, 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 oxide **(2)** and a mixture of 200 mL of 97% sulfuric acid. The reactant was dissolved and the reaction system then cooled to -5 °C with an ice/salt bath. Then a solution of 14.5 g (230 mmol) 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 a further 8 h. After that the reaction solution was hydrolyzed over 2 L of ice. When 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 25.70 g (70%) of yellow crystals of bis(3-nitrophenyl) phenyl phosphine oxide **(3)** 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 $\text{C}_{18}\text{H}_{13}\text{N}_2\text{OP}$: 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)

15.4 g (50 mmol) of bis(3-nitrophenyl) phenyl phosphine oxide **(3)** was placed into a 500-mL round-bottomed flask with 144 g of powder $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$, 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 that the solution was concentrated and then neutralized with a 25% NaOH aqueous solution. The solution obtained was then extracted with chloroform and the organic layer collected and concentrated under reduced pressure. Finally, the solid obtained was dried under reduced pressure and then 9.41 g (73%) of yellow crystals of bis(3-aminophenyl) phenyl phosphine oxide **(4)** were 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-d_6 , 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 $\text{C}_{18}\text{H}_{17}\text{N}_2\text{OP}$: C, 70.14; H, 5.51; N, 9.08; found: C, 70.71; H, 5.74; N, 8.91.

4,4'-Azodibenzoic acid (6)

4,4'-Azodibenzoic acid **(6)** was prepared according to a typical procedure, shown in Scheme 1.²⁴

Thirteen grams of 4-nitrobenzoic acid **(5)** (79 mmol) was heated in a solution of 50 g of sodium hydroxide in 250 mL of water at 50 °C. A solution of 100 g of glucose in 150 mL of water was added slowly at this temperature with occasional shaking. The reaction mixture was then cooled to ambient temperature and aerated for 8 h with vigorous stirring until orange-colored crystals were formed. The mixture was acidified with dilute acetic acid; then the liberated diacid was filtered, washed with water and dissolved in hot potassium carbonate solution to get an orange-colored solution. This solution was concentrated to get orange-colored crystals of potassium salt of diacid. On acidifying with dilute acetic acid, 18 g (86%) of rose-colored 4,4'-azodibenzoic acid **(6)** was obtained. mp > 300 °C, FT-IR (KBr): 3600-2900 (m, br), 1669

(s, br), 1614 (s), 1579 (s), 1410 (s), 1300-1200 (s, br), 1100-1000 (s, br), 868 (s), 777 (s) cm^{-1} . $^1\text{H-NMR}$ (90 MHz, DMSO-d_6 , TMS): δ 7.6-8.2 (m, 8H); 12.0 (br, 2H) ppm. Analysis: Calculated for $\text{C}_{14}\text{H}_{10}\text{N}_2\text{O}_4$: C, 62.24; H, 3.70; N, 10.36; found: C, 62.4; H, 3.8; N, 10.0.

Polymer synthesis

The polyamide **7** was prepared using the following procedure: 1 mmol of 4,4'-azodibenzoic acid (**6**) 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) of 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. Then the viscous reaction mixture was added to 25 mL of methanol. The precipitated polymer (**7**) was collected by filtration and was dried at $80\text{ }^\circ\text{C}$ for 8 h under vacuum to leave a brown solid.

Furthermore, polyamide **9** was prepared by the above procedure.

Results and Discussion

Monomer synthesis

Bis(3-aminophenyl) phenyl phosphine oxide (**4**) was prepared in 3 steps from simple organic compounds 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 $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$. Figure 1 displays the FT-IR 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.

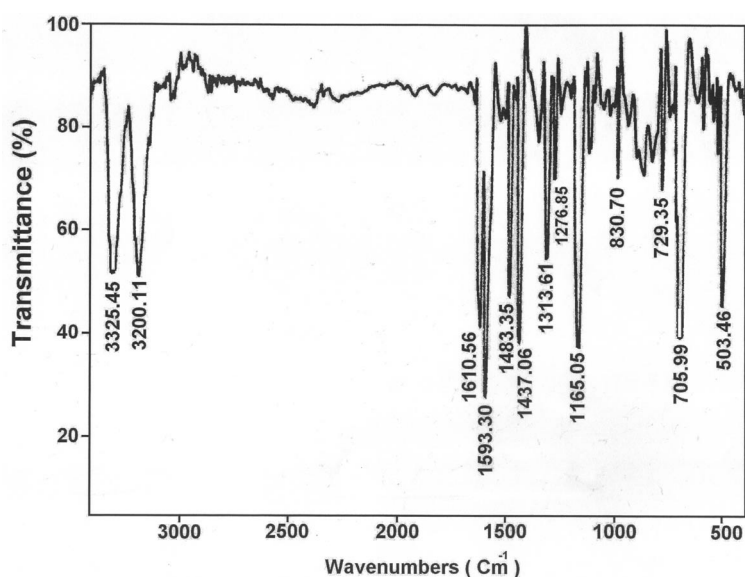


Figure 1. FT-IR spectrum of diamine **4**.

Figure 2 displays the $^1\text{H-NMR}$ spectrum of bis (3-aminophenyl) phenyl phosphine oxide (**4**). Peaks appearing at 5.30-5.40 ppm indicate the existence of amine groups (NH_2). Other peaks appearing at 6.55-7.55 ppm show 2 different aromatic rings in this compound.

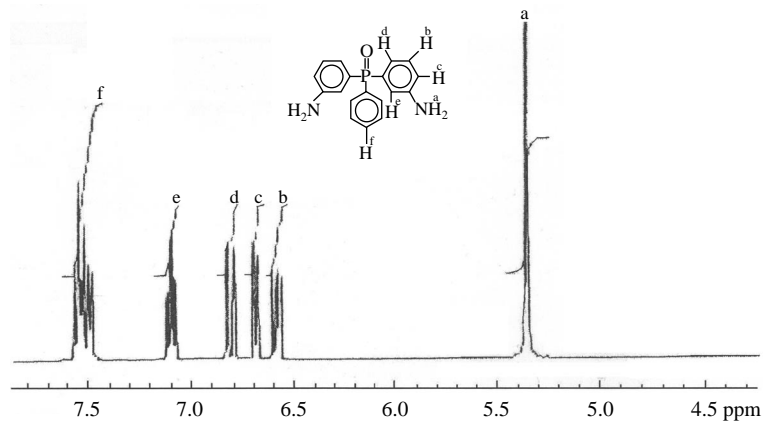
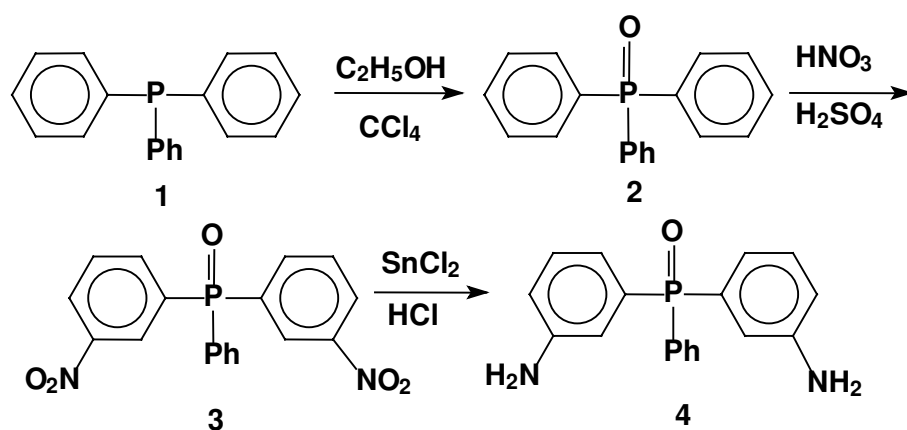
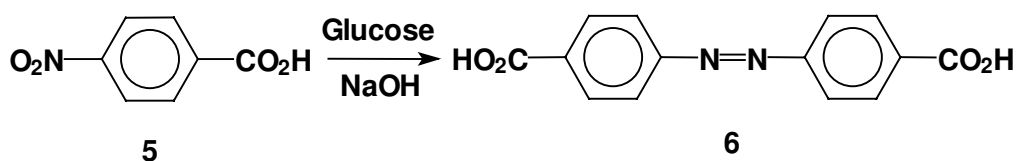


Figure 2. $^1\text{H-NMR}$ spectrum of diamine **4** (400 MHz).



Synthesis route for Bis(3-aminophenyl) phenyl phosphine oxide **4**



Synthesis route for 4,4'-Azobenzoic acid **6**

Scheme 1

Furthermore, 4,4'-azodibenzoic acid (**6**) was prepared by a reductive coupling reaction of 4-nitrobenzoic acid (**5**) in the presence of glucose in aqueous NaOH solution (Scheme 1). The chemical composition and purity of diacid (**6**) were also analyzed by $^1\text{H-NMR}$ and FT-IR spectroscopy, melting point and elemental analysis. Figure 3 displays the $^1\text{H-NMR}$ spectrum of 4,4'-azodibenzoic acid (**6**). Peaks around 7.6-8.2 ppm are related to aromatic hydrogens and the peak appearing at 12.0 ppm displays acidic hydrogen (COOH)

in this compound. The measured results in elemental analyses closely corresponded to the calculated ones, demonstrating that the expected compound was obtained.

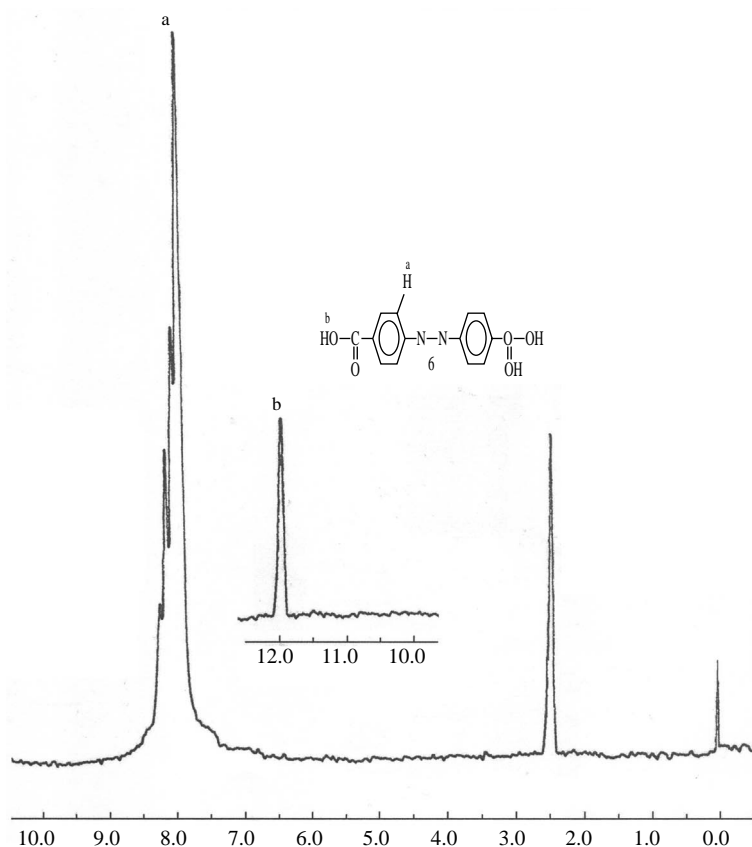
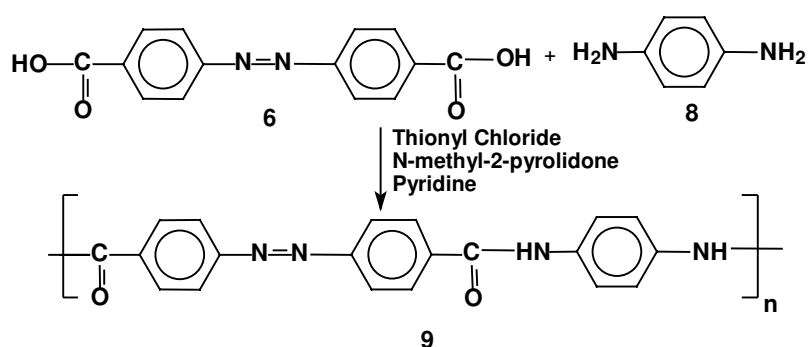
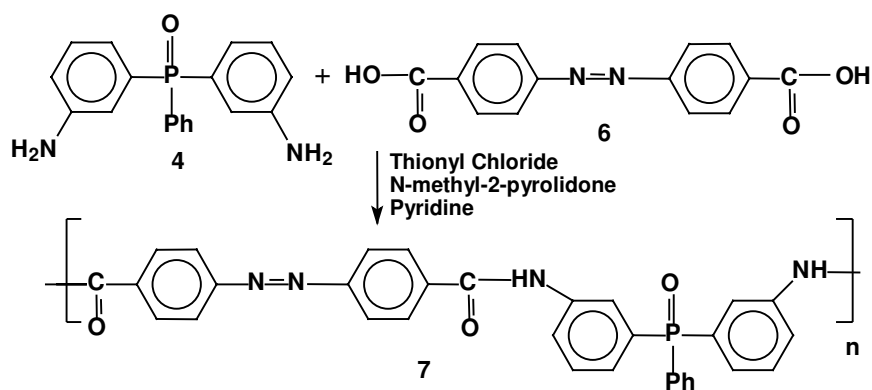


Figure 3. ¹H-NMR spectrum of diacid 6 (90 MHz).

The polyamide **7** was synthesized by polycondensation reaction of bis (3-aminophenyl) phenyl phosphine oxide (**4**) with 4,4'-azodibenzic acid (**6**) by using thionyl chloride, N-methyl-2-pyrrolidone and pyridine. To compare the flame retardance of polyamide (**7**), another polyimide (**9**) without phosphine oxide moiety was synthesized by direct polycondensation reaction of 4,4'-azodibenzic acid (**6**) with 1,4-phenylene diamine (**8**) using the same procedure (Scheme 2).

The polyamide **7** had an inherent viscosity of 0.55 dL/g. The structure of this polymer was confirmed as a polyamide by means of FT-IR spectroscopy and elemental analyses. The representative FT-IR spectrum of this compound is shown in Figure 4. The polymer showed an absorption band at 3313 cm⁻¹ due to N-H of the amide group. The absorption band at 1655 was related to the carbonyl of the amide group. Absorption bands around 1244 cm⁻¹ (P=O) and 1537 cm⁻¹ (P-Ph) corresponded 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.



Scheme 2

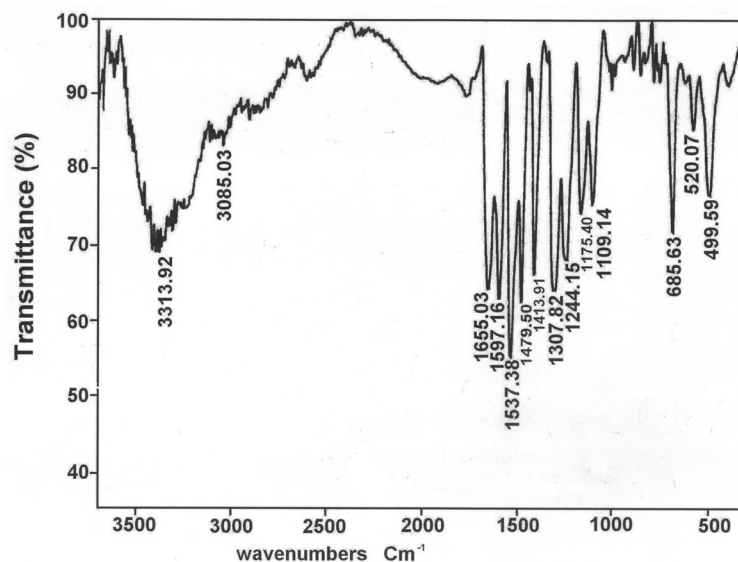


Figure 4. FT-IR spectrum of polyamide 7.

The solubility of polyamide **7** 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, methy-

lene chloride, methanol, ethanol and water. The thermal properties of polymers **7** and **9** were investigated by means of thermogravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min (Table 1). Initial decomposition temperature, 5% and 10% weight loss (T_5 , T_{10}) and char yields at 600 °C for these samples are summarized in Table 1.

Polyamide **7** exhibited good resistance to thermal decomposition up to 345-340 °C in nitrogen and began to decompose gradually above that temperature. The char yield for this polymer at 600 °C was 25% in nitrogen (Figure 5).

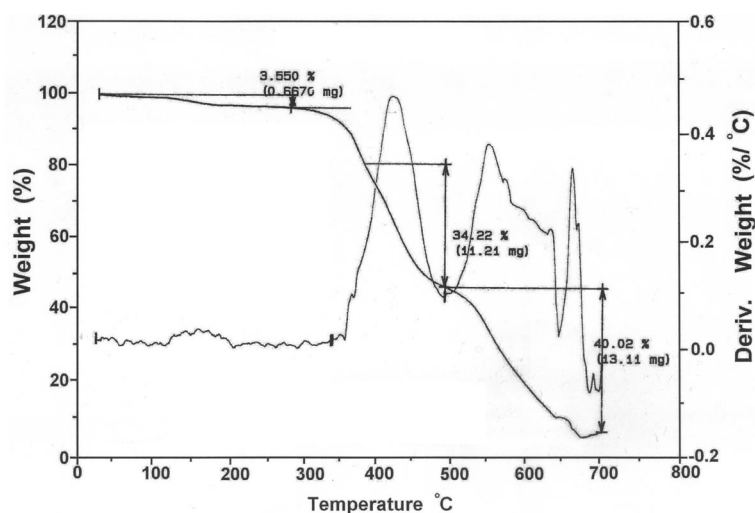


Figure 5. TGA & DTG of polyamide 7.

Table 1. Thermal behavior of polyamides **7** and **9**.

Polymer	$T_5(^{\circ}C)^a$	$T_{10}(^{\circ}C)^b$	Char Yield ^c	LOI ^d
7	345-350	375-380	25%	29
9	270-275	295-300	11%	20

^a and ^b: Temperature at which 5% or 10% weight loss respectively was recorded by TGA at a heating rate of 10 °C/min in N₂. ^c weight percentage of material left after TGA analysis at maximum temperature 600 °C in N₂. ^dLimiting Oxygen Index.

The flame retardance of these polymers was evaluated by measuring their LOI values (Table 1). Polyamide **7** showed good LOI data. Generally, materials exhibiting LOI values above 26 will show self-extinguishing behavior²⁶ and are considered flame retardant. Therefore, high char yield data along with a good LOI value in comparison to polyamide **9** indicated that this polymer had good flame retardance. The high LOI data and high char yield showed that the introduction of phosphine oxide and azobenzene moieties in the main chain caused flame retardance in polyamide **7**.

Conclusion

A new polyamide (**7**) containing phosphine oxide moiety in the main chain was synthesized by solution polycondensation reaction of an equimolar mixture of bis (3-aminophenyl) phenyl phosphine oxide (**4**) with 4,4'-azodibenzic acid (**6**). This polymer showed good solubility and thermal stability characterized by thermal gravimetric analysis (TGA and DTG). The introduction of phosphine oxide moiety into the

backbone of the polymer increased flame retardance. These properties can make this polymer attractive for practical applications such as processable high-performance engineering plastics.

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