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New Flame-Retardant Poly(ester-imide)s Containing Phosphine Oxide Moieties in the Main Chain: Synthesis and Properties

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Six new flame-retardant poly(ester-imide)s (**9a-f**) with high inherent viscosity and containing phosphine oxide moieties in the main chain were synthesized from the polycondensation reaction of N,N-(3,3-diphenylphenyl phosphine oxide) bistrimellitimide diacid chloride (**7**) with 6 aromatic diols (**8a-f**) by 2 different methods:–solution and microwave-assisted polycondensation. The results showed that compared to solution polycondensation, the microwave-assisted polycondensation reaction using a domestic microwave oven proceeded rapidly and was completed within about 9-12 min. All of the obtained polymers were fully characterized by means of elemental analysis, viscosity measurement, solubility testing, and FT-IR spectroscopy. Thermal properties and flame retardant behavior of the PEIs (**9a-f**) were investigated by using thermal gravimetric analysis (TGA and DTG) and the limited oxygen index (LOI). Data obtained by thermal analysis (TGA and DTG) revealed that these poly(ester-imide)s had good thermal stability. Furthermore, high char yields in TGA and good LOI values indicated that incorporating phosphine oxide moieties in the polymer backbone markedly improved their flame retardancy. These polymers can be potentially utilized in flame retardant thermoplastic materials.

Key Words: Flame-retardant polymers,;hosphine oxide moieties, N-(3,3-diphenylphenyl phosphine oxide) bistrimellitimide diacid chloride, romatic diols.

Introduction

During the last few decades, conventional materials such as metals, wood, glass, and ceramics have been increasingly replaced by synthetic polymers due to their versatility, low density, good mechanical and physical properties, and easy molding processes;[1] however, the advantages of polymeric materials are overshadowed by their easy combustibility and low stability in high temperatures, as compared to metals. More recently, considerable attention has been directed towards preparing flame-retardant polymers.[2−3] Among the flame-retardant polymers that were developed, phosphorus-containing polymers are the most widely used.[4−6] General types of phosphorus moieties have been incorporated into different polymeric backbones, such as epoxy resin, polyurea, polyamide, poly(vinyl chloride), polyester, polyimide, polypropylene, and polyether.[7−15] Among the polymers with phosphorus moieties, those with phosphine oxide moieties have major advantages, including good flame-retardant properties, high thermal oxidative stability, enhanced solubility in organic solvents, improved miscibility, and good adhesion to other compounds.[16−18]

Recently, there has been growing interest in applying microwave energy to synthetic organic chemistry, sample preparation for analysis, extraction of natural products from plants, waste treatment, and polymer synthesis.[19−27] Such reactions proceed very rapidly and are completed within a short period of time. Recently, we used microwave irradiation for the synthesis of poly(amide-imide)s and poly(ester-imide)s.[28−32]

In the present research, 6 new flame-retardant poly(ester-imide)s (**9a-f**) were prepared by polycondensation reaction of N,N-(3,3-diphenylphenylphosphine oxide) bistrimellitimide diacid chloride (**7**) with hydroquinone (**8a**), resorcinol (**8b**), 2,7-dihydroxynaphthalene (**8c**), bis(4-hydroxyphenyl) sulfone (**8d**), 2,2-bis(4-hydroxyphenyl) propane (**8e**), and 1,4-dihydroxyantraquinone (**8f**) by 2 different methods:–solution and microwave-assisted polycondensation.

Experimental

Chemicals were purchased from Fluka Chemical Co. (Switzerland), Aldrich Chemical Co. (Milwaukee, WI, USA), and Merck Chemical Co. (Germany). Fourier transform infrared (FTIR) spectra were recorded on a Galaxy series FTIR 5000 spectrometer (UK). KBr pellets were used to obtain the spectra of solids. Vibrational transition frequencies were reported in wave number (cm^{-1}). Band intensities were characterized as weak (w), medium (m), shoulder (sh), strong (s), and broad (br). Inherent viscosity was measured by a standard procedure using a Technico® Viscometer. Thermal gravimetric analysis (TGA and DTG) data of the polymers were obtained on a Mettler TA4000 system under N_2 atmosphere at a rate of 10 °C/min. Elemental analyses were performed by the Arak Petrochemical Company, Arak, Iran. The limited oxygen index (LOI) was measured with a Stanton Redcraft flame meter. A Samsung domestic microwave oven (2450 MHz, 900 W) was used for carrying out the polycondensation reactions.

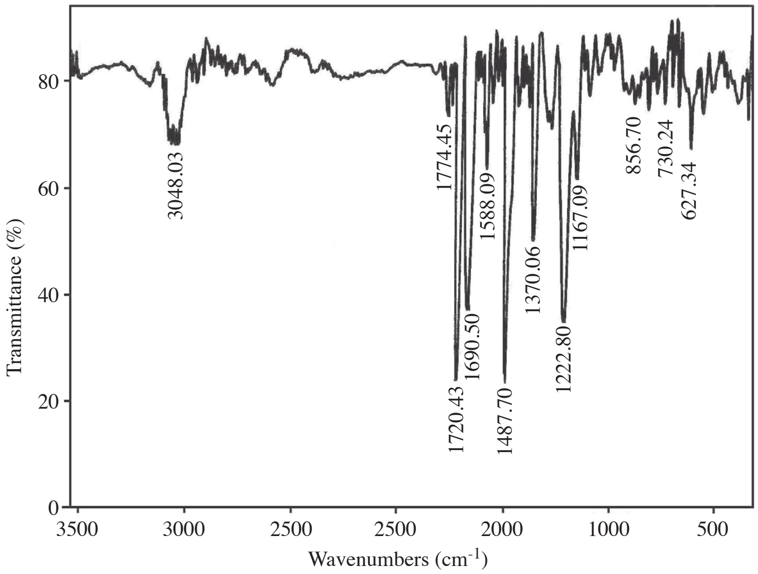
Monomer Synthesis

N,N-(3,3-diphenylphenylphosphine oxide) bistrimellitimide diacid chloride (**7**) was prepared according to a typical procedure as shown in Scheme 1.[33,34]

Polymer Synthesis

Poly(ester-imide) (9a) was prepared from the reaction of N,N-(3,3-diphenylphenyl phosphine oxide) bistrimellitimide diacid chloride (7) with hydroquinone (8a) by 2 different methods.

Method A. Solution polycondensation with pyridine as a base:;.11 g (1 mmol) of hydroquinone (**8a**) and 8 mL of DMAc were placed into a 25-mL round-bottomed flask with a stirring bar. The mixture was cooled in an ice water bath and 0.32 g (4 mmol) of pyridine was added to this solution. Then, 0.69 g (1 mmol) of N,N-(3,3-diphenylphenylphosphine oxide) bistrimellitimide diacid chloride (**7**) was added all at once. Polymerization proceeded as the acid chloride was dissolved. The reaction mixture was stirred in an ice water bath for 1 h and then the cooling bath was removed and the stirring continued overnight at room temperature, followed by heating at 80 °C for 12 h. The reaction mixture was poured into 50 mL of methanol and then the precipitated polymer was collected by filtration, washed thoroughly with methanol, and dried at 80 °C for 12 h under vacuum to leave 0.59 g (81%) of polymer (**9a**).



Scheme 1.

Method B. Polymerization by microwave irradiation in a porcelain dish:;n equimolar mixture of 0.69 g (1.0 mmol) of N,N-(3,3-diphenylphenylphosphine oxide) bistrimellitimide diacid chloride (**7**) and 0.11 g (1.0 mmol) of hydroquinone (**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. The reaction mixture was then 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 0.67 g (92%) of solid polymer (**9a**).

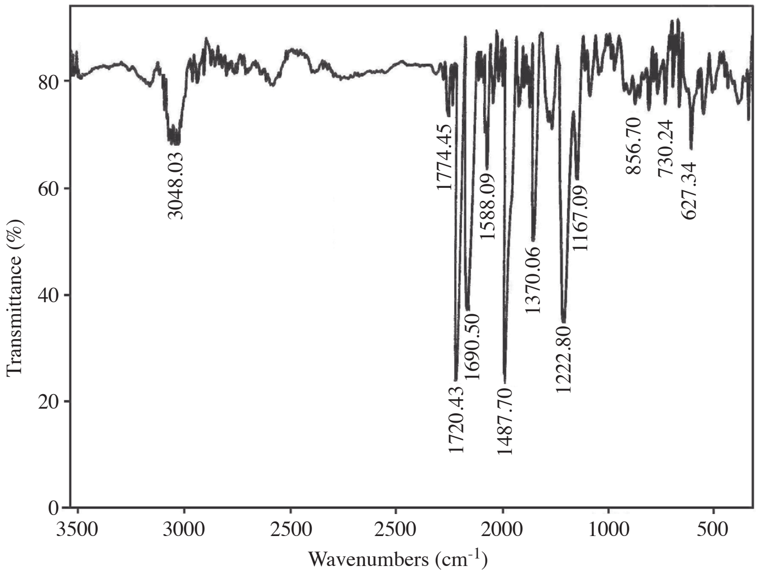
Results and Discussion

Monomer Synthesis

N,N-(3,3-diphenylphenylphosphine oxide) bistrimellitimide diacid chloride (**7**) was prepared in a 5-step reaction of a simple organic compound of triphenyl phosphine (**1**), as shown in Scheme 1.[33,34] At first, a diamine compound (**4**) with phosphine oxide moiety was obtained, and then diimide-acid (**6**) was synthesized by condensation reaction of 2 equimolar amounts of trimellitic anhydride (**5**) with 1 equimolar amount of diamine (**4**) in a mixture of acetic acid-pyridine (3:2). After evaporation of the solvent and dissolving the residue in cold water, a gum-like solid was obtained that broke up in a concentrate of HCl and gave a white-yellow solid when recrystallized with DMF-H_2O. The resulting diimide-acid (**6**) was then 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 recrystallization with extra-pure tetrahydrofuran.

Polymer Synthesis

PEIs (9a-f) were synthesized by microwave-assisted polycondensation and by solution polycondensation reactions of an equimolar mixture of monomer (7) with 6 different derivatives of aromatic diols (8a–f) as shown in Scheme 2.



Scheme 2.

The microwave-assisted polycondensation reactions were carried out in a porcelain dish in the presence of a small amount of o-cresol, which was used as a polar organic medium that acts as a primary microwave absorber, and as a solvent for both of the starting monomers and the resulting polymers. This allowed the reaction mixture to be uniformly heated and, thereby, the subsequent polycondensation reaction occurred, leading to the high-yield polymer formation. The optimum reaction time (irradiation time) was between 9 and -12 min. With a reaction time less than 9 min the polymers obtained will have lower inherent viscosities and with a reaction tine more than 12 min the materials will be degraded. The reaction yields and some physical data of the polymers that were obtained with this method are listed in Table 1. Furthermore, we compared the microwave-assisted polycondensation method with the conventional solution polycondensation method, and the polymerization reaction of diacid chloride **(7)** with 6 different derivatives of aromatic diols **(8a–f)** was performed in DMAc solution in the presence of pyridine as a base. Although we obtained a high yield of PEIs **(9a–f)**, low inherent viscosities were the result; therefore, microwave-assisted polycondensation proceeded rapidly and the products had higher inherent viscosity in a shorter period of time, as compared to solution polycondensation.

Polymer Characterization

The reaction yields and some physical data of these polymers are listed in Table 1 (microwave irradiation) and Table 2 (solution polycondensation). PEIs **(9a-f)** derived from monomer (**7**) were different colors, ranging from yellow to brown. As shown in Table 1, these polymers were obtained in quantitative yields with inherent viscosities between 0.40 and 0.56 dL/g. The structures of these polymers were confirmed as

PEIs by means of FT-IR spectroscopy and elemental analysis. The representative FT-IR spectrum of PEI **(9b)** is shown in Figure 1.

The polymer exhibited characteristic absorption bands at 1774 and 1720 cm^{--1} for the imide ring (asymmetric and symmetric C=O stretching vibrations), 1370 cm^{--1} (C-N stretching vibration), and 1167 and 730 cm^{--1} (imide ring deformations). The absorption bands of the ester groups appeared at 1690 cm^{-1} (C=O stretching) and 1222 cm^{-1} (C-O stretching)$^{-}$.

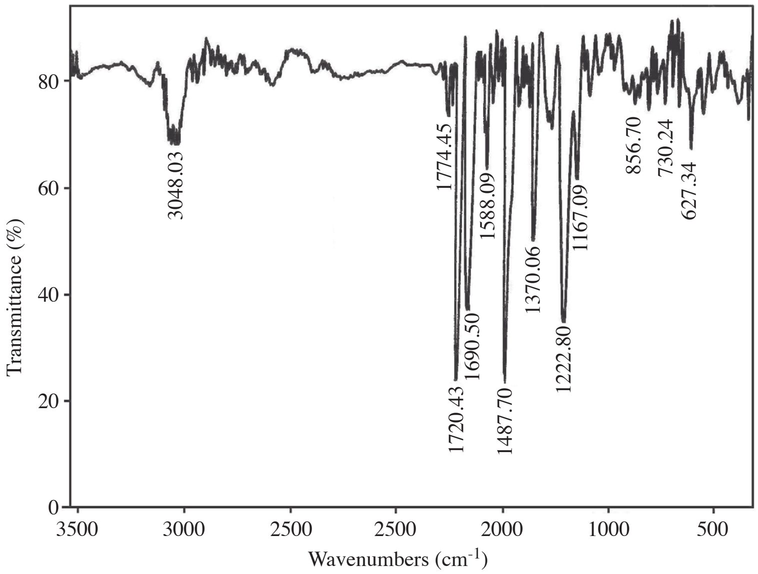


Figure 1. FT-IR spectrum of PEI **9b**.

Table 1. Synthesis and some physical properties of PEIs **(9a-f)** by microwave irradiation.

Aromatic Diols	Polymer	Yield (%)	Time (min)^{a}	η_{inh}(dL/g)^{b}	Colors
8a	**9a**	90	9	0.40	Light gray
8b	**9b**	92	10	0.56	Light gray
8c	**9c**	89	10	0.50	Brown
8d	**9d**	88	9	0.45	Brown
8e	**9e**	90	11	0.55	Dark brown
8f	**9f**	94	12	0.43	Dark red

[a] Duration of irradiation by microwave oven. [b] Measured at a concentration of 0.5 g/dL in DMF at 25 °C.

Elemental analysis of the resulting PEIs **(9a-f)** was in good agreement with the calculated values for the proposed structures (Table 3).

The solubility of PEIs **(9a–f)** was investigated as 0.01 g of polymeric sample in 2 mL of solvent. All of the polymers were soluble in organic solvents such as DMF, DMAc, DMSO, and NMP at room temperature, and were insoluble in solvents such as chloroform, methylene chloride, methanol, ethanol, and water. The high solubility of the obtained PEIs was apparently due to the introduction of an m-phenylene structure and phosphine oxide linkages, which resulted in increasing the free volume between the polymer chains and decreasing intermolecular interactions.

Table 2. Synthesis and some physical properties of PEIs **(9a-f)** by solution polycondensation.

Aromatic Diols	Polymer	Yield (%)	η_{inh}(dL/g) [a]	Colors
8a	**9a**	79	0.29	Light gray
8b	**9b**	81	0.34	Light gray
8c	**9c**	83	0.23	Brown
8d	**9d**	84	0.22	Brown
8e	**9e**	80	0.21	Dark brown
8f	**9f**	78	0.30	Dark red

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

Table 3. Elemental analysis of PEIs **(9a-f)**.

Polymer	Formula		C%	H%	N%
9a	$C_{42}H_{23}N_2O_9P$	calcd.	69.05	3.14	3.83
	$(730.42)_n$	observed	68.0	2.6	2.4
9b	$C_{42}H_{23}N_2O_9P$	calcd.	69.05	3.14	3.83
	$(730.42)_n$	observed	68.2	2.6	2.8
9c	$C_{46}H_{25}N_2O_9P$	calcd.	70.78	3.20	3.58
	$(780.46)_n$	observed	69.2	2.2	2.9
9d	$C_{51}H_{33}N_2O_9P$	calcd.	72.18	3.88	3.29
	$(848.51)_n$	observed	71.6	2.8	2.5
9e	$C_{48}H_{27}N_2O_{11}SP$	calcd.	66.22	3.10	3.21
	$(870.54)_n$	observed	64.9	2.5	2.6
9f	$C_{50}H_{25}N_2O_{11}P$	calcd.	69.78	2.90	3.25
	$(860.50)_n$	observed	68.1	2.0	2.5

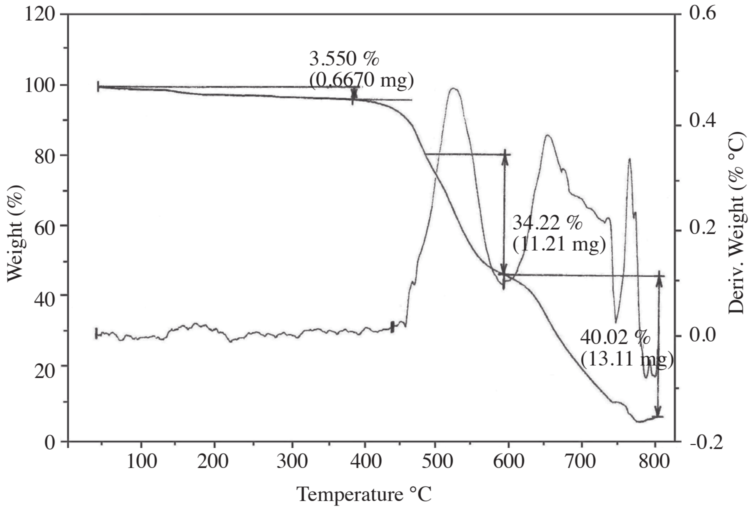


Figure 2. TGA and DTG thermogram of PEI **9c**.

Thermal Properties

The thermal properties of 3 PEIs, (**9a**), (**9c**), and (**9f**), were investigated by means of thermo gravimetric analysis (TGA) and derivative thermogravimetric (DTG) analysis in a nitrogen atmosphere at a heating rate of 10 °C/min (Figures 2 and 3).

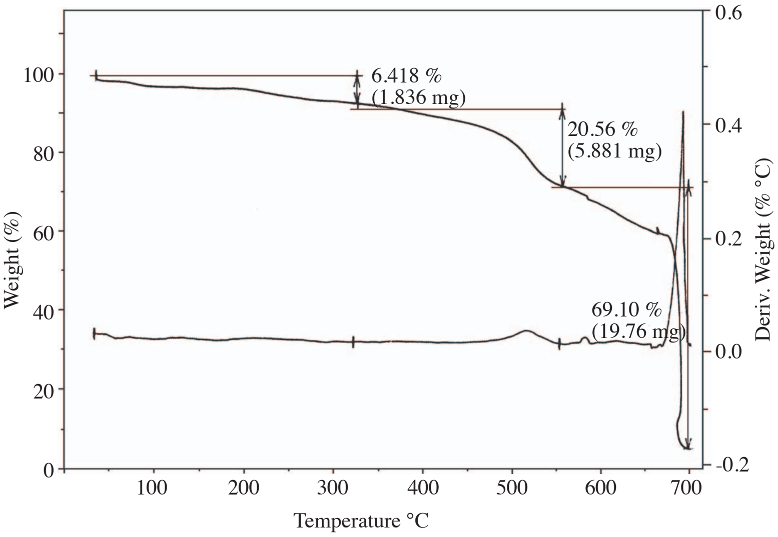


Figure 3. TGA and DTG thermogram of PEI **9f**.

Initial decomposition temperature, 5% and 10% weight loss temperature (T_5, T_{10}), and char yields at 600 °C are summarized in Table 5. These polymers exhibited good resistance to thermal decomposition up to 350-450 °C in nitrogen and began to decompose gradually above that temperature. The temperature of 5% weight loss for all the polymers ranged between 355 and 455 °C, and the residual weight at 600°C ranged from 48% to 62% in nitrogen. The high char yields of these polymers at high the temperature region were important, showing that these polymers had good thermal stability.

Table 4. Thermal behavior and LOI analysis data of PEIs (**9a**), (**9c**), and (**9f**).

Polymer	T_5 (°C)^a	T_{10} (°C)^b	Char Yield^c (%)	LOI^d
9a	350-355	365-370	50	27
9c	400-405	445-450	48	28
9f	335-340	435-440	67	31

^{a,b}Temperature at which 5% or 10% weight loss was recorded by TGA at a heating rate of 10 °C/min in N_2.^{c}Percent of weight of material that remained after TGA analysis at the maximum temperature of 600 °C in N_2.

Additionally, the flame-retardant property of these polymers was evaluated by measuring their LOI values, which were between 27 and 31. Generally, materials exhibiting LOI values above 26 should demonstrate self-extinguishing behavior[35] and are considered to be flame retardant; therefore, the high char yields and good LOI values (27-31) indicate that these polymers had good flame-retardant properties.

Conclusions

A new series of PEIS **(9a-f)** containing phosphine oxide moieties were synthesized by 2 different methods–microwave-assisted polycondensation and solution polycondensation reactions of an equimolar mixture of monomer **7** with 6 different derivatives of aromatic diols **(8a–f)**. These polymers showed good solubility and thermal stability, as determined by thermal gravimetric analysis (TGA and DTG). The high char yields and good LOI values of these polymers show that the introduction of phosphine oxide moieties into the backbone increased thermal stability and demonstrated the polymers' flame-retardant property. These properties can make these polymers attractive for practical applications, such as processable high-performance engineering plastics. In addition, the results of the present study demonstrate that microwave irradiation was a valuable optimization method, as it dramatically reduced reaction time and increased the inherent viscosity of the obtained polymers. We are currently using this method for the synthesis of novel polymers and the modification of polymers.

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