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Synthesis and properties of aromatic ether phosphine oxide containing oligomeric phthalonitrile resins with improved oxidative stability

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Abstract

A series of multiple aromatic ether-linked phthalonitrile resins containing an aromatic ether phosphine oxide group in the backbone have been synthesized and characterized. The oligomeric phthalonitrile monomers were prepared from the reaction of an excess amount of either bisphenol A or resorcinol with bis(4-fluorophenyl)phenylphosphine oxide in the presence of K_2CO_3 in a *N*,*N*-dimethylformamide/toluene solvent mixture, followed by reacting with 4-nitrophthalonitrile in a two-step, one-pot reaction. Rheometric measurements and thermogravimetric analysis of the cured resins showed that the oligomeric phthalonitrile resins maintained good structural integrity upon heating to elevated temperatures and exhibited excellent thermal properties. When subjected to long-term oxidative exposures, the phosphorus-containing phthalonitriles showed superior performance and less oxidative damage compared to other aromatic-containing phthalonitrile resins. Scanning electron spectroscopy studies showed the formation of microcracks during the oxidative aging at elevated temperatures.
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Keywords: Aromatic ether; Phthalonitrile; Curing

1. Introduction

High temperature polymers are important materials with a variety of aerospace, marine, and microelectronic uses [1–3]. Polymeric/organic based materials have significant weight [1] and performance advantages relative to metals. For composite applications, it is essential to have resin systems that are liquids or have fairly low melting points, exhibit a large processing window defined as the difference between the melting point and the polymerization temperature, and have a low viscosity for fabrication of composite components by cost effective methods such as resin transfer molding, resin infusion molding, and filament winding.

Phthalonitrile resins have been thoroughly studied over the past 25 years and are a unique class of high temperature materials having a variety of potential uses for adhesive [4], electronic [5–7], and structural applications [8–10]. These resins have superior flame resistant properties when compared to other polymeric materials [8,9]. A variety of high temperature materials have been developed by incorporating aromatic units within polymeric systems containing phthalonitrile [11–14] end units. Recent research in this area has focused on the incorporation of oligomeric aromatic ether-containing linkages between the terminal phthalonitrile units [15–18]. Our efforts have resulted in the design and synthesis of novel oligomeric aromatic ether-containing phthalonitrile resin systems by utilizing a nucleophilic displacement reaction. These new phthalonitrile monomers have been prepared utilizing a two-step, one-pot reaction. Employing this synthetic method to form oligomeric and not pure compounds, the new phthalonitriles have improved processability at lower temperatures. Our synthetic approach results in a phthalonitrile system with a low melting point and a broad processing window for easy conversion to crosslinked polymers [15–18]. These properties allow phthalonitrile resins to compete with other high performance polymeric systems.

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The key to the development of high temperature polymers with good oxidative stability is the incorporation of thermally stable structural units such as aromatic and heteroaromatic rings or units such as silicon, oxygen, and phosphorus within the backbone of a polymeric system. Many high temperature systems containing aromatic ether phosphine oxide units within the polymeric structure have been developed over the last 30 years including polyimides [19], polyethers [20], and polycyanurates [21,22]. These systems show enhanced thermal properties and better stability under oxidative conditions.

This paper will show the synthesis, polymerization, and some material properties of a series of newly developed phthalonitrile resins, which incorporate aromatic ether phosphine oxide units into the oligomeric backbone. By utilizing a simple nucleophilic displacement reaction, easily processable/low melting phthalonitrile resins can be readily produced. These resins show superior oxidative stability when compared to other phthalonitrile resins, which do not contain a phosphorous moiety.

2. Experimental section

All starting materials were of reagent grade and used without further purification. Differential scanning calorimetric (DSC) analysis was performed on a TA Instruments DSC 2920 modulated thermal analyzer at a heating rate of 10 °C min^{-1} and a nitrogen purge of 50 $\text{cm}^3\ \text{min}^{-1}$. Thermogravimetric analysis (TGA) was performed on a TA Instruments TGA Q50 at a heating rate of 10 °C min^{-1} under a nitrogen or air purge of 100 $\text{cm}^3\ \text{min}^{-1}$. Infrared (IR) spectra were recorded on films deposited on NaCl plates using a Nicolet Magna FTIR 750 spectrometer. ^{1}H NMR was performed on a Brüker ADVANCE 300 spectrometer. Scanning electron microscopy (SEM) studies were performed on samples, which were attached onto clean silicon wafers using epoxy resin, and the images were taken on a Zeiss Model Supra 55 electron microscope at 5 kV.

2.1. Rheometric measurements

A TA Instruments AR-2000 Rheometer, in conjunction with an environmental testing chamber for temperature control and torsion fixtures, was used to monitor the response of polymeric samples (50 mm × 13 mm × 2 mm) to oscillatory testing. The measurements were made under nitrogen over the temperature range of ~40–400 °C. A temperature ramp of 3 °C min^{-1} was used to determine the storage modulus and damping factor (tan δ) of the material at a frequency of 1 Hz and a strain of $2.5 \times 10^{-2}\%$. Normal force control was utilized throughout the tests to keep the samples taut.

2.2. Synthesis of the oligomeric multiple aromatic ether containing phthalonitrile (*1a*)

To a 100 mL three-necked flask fitted with a thermometer, a Dean–Stark trap with condenser, and a nitrogen inlet were added resorcinol (**2a**) (5.00 g, 45.4 mmol), bis(4-fluorophenyl)phenylphosphine oxide [20] (**3**) (7.14 g, 22.7 mmol), powdered anhydrous K_2CO_3 (12.6 g, 91.0 mmol), toluene (10 mL), and *N*,*N*-dimethylformamide (DMF) (50 mL). The resulting mixture was degassed with argon at ambient temperature and the Dean–Stark trap was filled with toluene. The mixture was refluxed at 135–145 °C under an argon atmosphere for 12–18 h or until no more water was observed being collected in the Dean–Stark trap. FTIR spectroscopy was used to confirm and monitor the formation of the desired oligomeric product. Toluene was then removed by distillation and the reaction mixture was cooled to 50 °C. At this time, 4-nitrophthalonitrile (**5**) (7.91 g, 45.7 mmol) was added in one portion and the reaction mixture was heated at 80 °C for 6–8 h. The mixture was allowed to cool to ambient temperature and poured into a 5% aqueous HCl solution resulting in the formation of a solid. The material was broken up and collected using a Bűchner funnel. The white solid was dissolved in chloroform (200 mL) and washed with 200 mL of a 5% aqueous KOH solution, with 200 mL of distilled water until neutral, with 200 mL of a 5% aqueous HCl solution, and finally with 200 mL of water until neutral. The solvent was removed *in vacuo* and the yellowish-orange amorphous solid ($T_g = 75$ °C) was vacuum dried to yield **1a** (15.8 g, 93%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.59–7.39 (m, aromatic-H), 7.30–7.20 (m, aromatic-H), 7.06–6.94 (m, aromatic-H), 6.82–6.72 (m, aromatic-H). IR [cm^{-1}]: ν 3075 (C=CH), 2232 (CN), 1585 (C=C), 1477 (aromatic), 1308 (aromatic), 1244 (C–O), 1172 (C–O), 1122 (P=O), 975 (C–O), 837 (aromatic).

2.3. Synthesis of the oligomeric multiple aromatic ether containing phthalonitrile (*1b*)

In a procedure analogous to **1a**, bisphenol A (**2b**) (5.00 g, 21.9 mmol), bis(4-fluorophenyl)phenylphosphine oxide [20] (**3**) (3.49 g, 11.1 mmol), powdered anhydrous K_2CO_3 (7.55 g, 54.7 mmol), and 4-nitrophthalonitrile (**5**) (3.87 g, 22.4 mmol) were reacted in toluene (10 mL) and *N*,*N*-dimethylformamide (DMF) (40 mL). The product **1b** (9.89 g, 91%) was isolated as a red amorphous solid ($T_g = 90$ °C). ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.61–7.52 (m, aromatic-H), 7.43–7.31 (m, aromatic-H), 7.34–7.19 (m, aromatic-H), 7.02–6.92 (m, aromatic-H), 1.75–1.66 (m, CH_3). IR [cm^{-1}]: ν 3058 (C=CH), 2969 (CH_3), 2231 (CN), 1589 (C=C), 1491 (aromatic), 1281 (CH_3), 1248 (C–O), 1173 (C–O), 1117, (P=O), 970 (C–O), 834 (aromatic).

2.4. Preparation of monomer/amine mixtures for DSC analysis

To the melt of monomers **1a** or **1b** at 200 °C was added 3 wt% of bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS). Once the curing additive had been evenly dispersed by stirring for 2 min, the sample was cooled and used in the DSC studies.

2.5. Sample preparation for rheometric measurements

Samples for rheometric measurements were prepared by degassing monomers **1a** or **1b** under vacuum at 250 °C for

4 h in a mold with cavity dimensions of 50 mm × 13 mm. The temperature of the mold was reduced to 200 °C, bis[4-(4-aminophenoxy)phenyl]sulfone (*p*-BAPS) (3 wt%) was added with stirring, and the resulting mixtures were degassed for an additional 30 min. The samples were cooled, placed in an oven, and heated under argon at 270 °C for 12 h (overnight), 300 °C for 4 h, 350 °C for 4 h, and 375 °C for 8 h. The cured polymers **6a** or **6b** were removed from the mold and sanded to a thickness of approximately 2 mm.

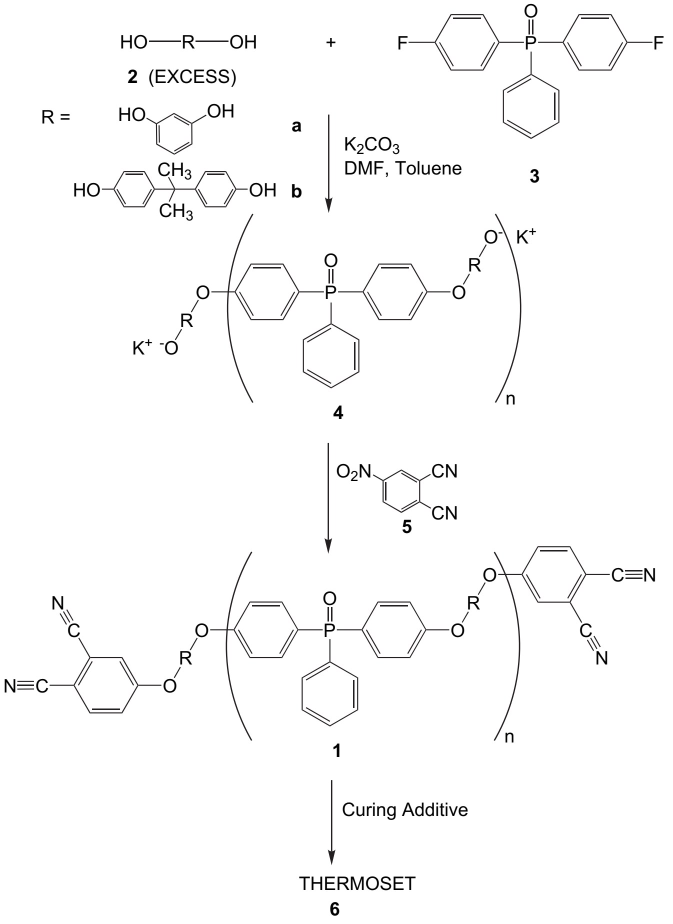
*2.6. Polymerization and TGA studies on thermosets **6a** and **6b***

Samples containing **1a** or **1b** and 3 wt% of *p*-BAPS were stirred at 200 °C for 2 min and cured under nitrogen by heating in a TGA pan at 270 °C for 12 h (overnight), 300 °C for 4 h, 350 °C for 4 h, and 375 °C for 8 h to afford polymers **6a** and **6b**, as films on the bottom of the pan. The thermal and thermo-oxidative properties of the polymer films were then determined from 25 to 1000 °C by TGA analysis. Long-term oxidative stability studies were performed on polymer films from 250 to 400 °C in 8 h temperature segments.

3. Results and discussion

The synthesis of two multiple aromatic ether-linked phthalonitriles **1a** and **1b**, which contain an aromatic ether phosphine oxide unit in the backbone, has been achieved by a nucleophilic displacement reaction utilizing an activated halogen containing compound, bis(4-fluorophenyl)phenylphosphine oxide **3** [20] (Scheme 1). The potassium diphenolate-terminated intermediate **4** was prepared from the reaction of **2** and **3** in the presence of potassium carbonate as the base in a DMF/toluene solvent mixture. This allows the azeotropic distillation of the water formed as a by-product in the reaction at temperatures between 135 and 145 °C. Once no more water was observed being azeotropically distilled and infrared (IR) spectroscopy confirmed the desired oligomeric product [16–18], the reaction was considered complete. Further reaction of **4** with 4-nitrophthalonitrile **5** afforded oligomeric phthalonitriles **1a** and **1b**, which were readily soluble in common organic solvents such as toluene, DMF, acetone, methylene chloride, ether, and chloroform, in 91 and 93% yields, respectively. The structures of the two monomers were confirmed by IR and ^{1}H NMR spectroscopies. The length of the spacer between the terminal phthalonitrile groups can be varied by changing the ratio of **2** (excess) and **3**.

The neat curing of phthalonitrile resins has been shown to proceed very slowly even during extended periods at temperatures in excess of 400 °C [23,24]. Therefore, it is necessary to incorporate a curing additive to initiate the curing process more effectively. To allow the thermosetting reaction to proceed at a fairly low temperature, bis[4-(4-aminophenoxy)-phenyl]sulfone (*p*-BAPS, 3 wt%) was added to the phthalonitrile monomers **1a** and **1b** with stirring at 150 °C. By heating to 150 °C, the viscosity of **1** was substantially reduced, which permitted easy mixing of the curing additive. *p*-BAPS was chosen as the curing additive because of its thermal stability at the initial processing or curing temperature (~200 °C) [25].



Scheme 1. Synthesis of oligomeric phthalonitrile **1** and thermoset **6**.

Polymerization studies of **1a** and **1b** ($n = 1$) were achieved by DSC analyses up to 400 °C in the presence of 3 wt% of *p*-BAPS [24,25] to afford **6a** and **6b**, respectively. The DSC thermogram (Fig. 1) of monomer **1a** revealed a glass transition (T_g) at approximately 75 °C and an exothermic transition

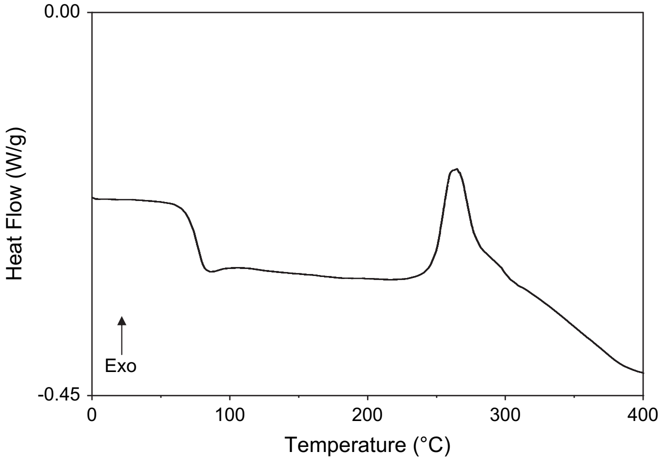


Fig. 1. DSC thermogram of monomer **1a** cured with 3 wt% *p*-BAPS.

peaking at 260 °C attributed to the reaction with *p*-BAPS. For **1b**, similar such peaks appeared at 90 and 245 °C. Monomers **1a** and **1b**, which exhibited low softening temperatures, were completely free flowing at around 150 °C (as determined by a visual melting test), and had a long processing window (~100 °C) before reaction with the curing additive occurred at about 230 °C. Monomer **6a** had a lower T_g relative to **6b** which we have observed before for systems of similar structure [17,18].

Rheometric measurements were performed up to 400 °C on a sample of **6a** cured with 3 wt% *p*-BAPS (Figs. 2 and 3). The sample showed no visible changes characteristic of a viscoelastic transition to a rubbery state. However, the storage modulus gradually decreased from ambient temperature to 400 °C indicating flexibility and mobility within the thermoset during the thermal treatment. This mobility does not result in catastrophic mechanical failure. The storage modulus for **6a** changed from 2780 to 580 MPa when heated from 30 to 400 °C. The reduction in modulus values gradually changed to about 700 MPa at 325 °C. From 325 to 400 °C, a much slower change in the modulus was observed. Fig. 3 shows the damping factor (tan *δ*) for polymer **6a** cured up to 400 °C. The damping plot shows two minor transitions peaking at about 98 and 177 °C and a broader transition leveling off above 300 °C. These minor transitions are probably attributed to some mobility within the backbone of **6a**. When polymer **6b** was cured under identical conditions, a similar mechanical behavior was observed.

The thermal and thermo-oxidative properties of polymer **6** were investigated between 25 and 1000 °C using TGA analysis. Figs. 4 and 5 show the TGA thermograms for **6a** and **6b** cured to 375 °C with 3 wt% *p*-BAPS. Polymers **6a** and **6b** retained 95% weight at around 490 °C and exhibited char yields of 65 and 56%, respectively, upon heating to 1000 °C under an inert atmosphere. Samples of **6a** and **6b** heated under a flow of air showed a weight retention of 95% at 490 and 495 °C, catastrophic decomposition occurring between 600 and 800 °C, and a weight retention of 4.3 and 8.0% at 1000 °C.

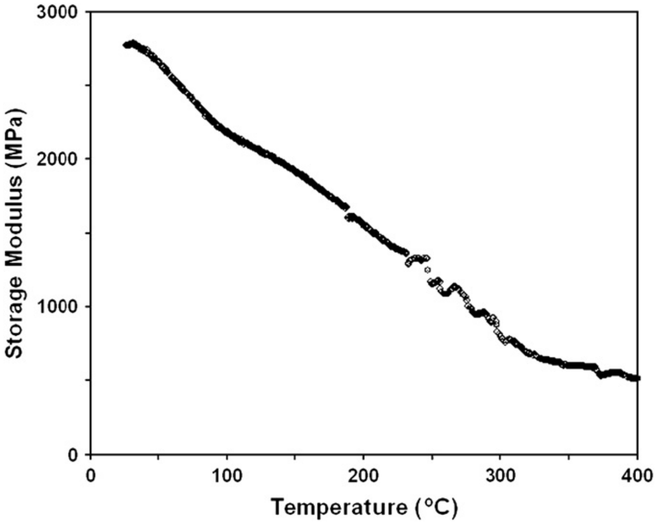


Fig. 2. Storage modulus for polymer **6a** cured with 3 wt% *p*-BAPS up to 400 °C.

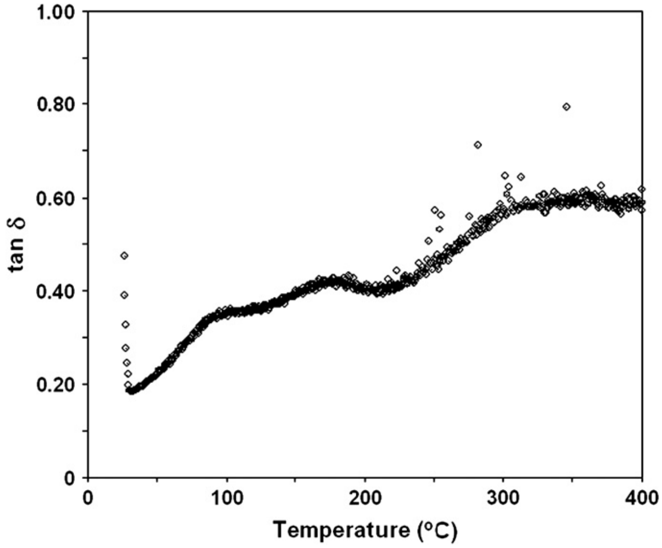


Fig. 3. Damping factor (tan *δ*) for polymer **6a** cured with 3 wt% *p*-BAPS up to 400 °C.

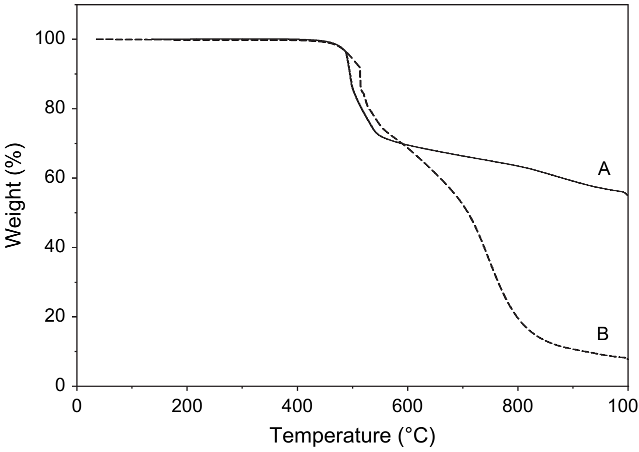


Fig. 4. TGA thermograms of polymer **6a** heated to 1000 °C: under nitrogen (A) and under air (B).

The oxidative stability for polymers **6a** and **6b** was examined over an extended period at elevated temperatures. Figs. 6 and 7 show oxidative aging plots for **6a** and **6b** heated stepwise at a variety of temperatures in air at 8 h temperature intervals. Table 1 indicates the percentage of total cumulative weight loss at various temperatures. As a comparison, the oxidative aging data for resins **7a** and **7b** [17,18] (Fig. 8), which are produced by the same reaction scheme but do not contain phosphorus atoms in the backbone, were included in Table 1 and in Figs. 6 and 7. Upon heating from 250 to 375 °C, a cumulative weight loss of 3.9 and 4.2% was observed for polymers **6a** and **6b**, respectively. These results were a slight improvement, especially for the resin which contained the bisphenol A moiety, over previously developed oligomeric phthalonitrile resins **7a** and **7b** where 4.0 and 7.2% weight losses

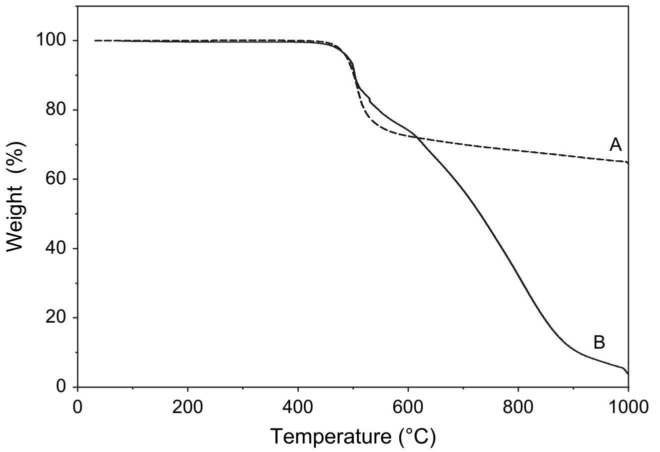


Fig. 5. TGA thermograms of polymer **6b** heated to 1000 °C: under nitrogen (A) and under air (B).

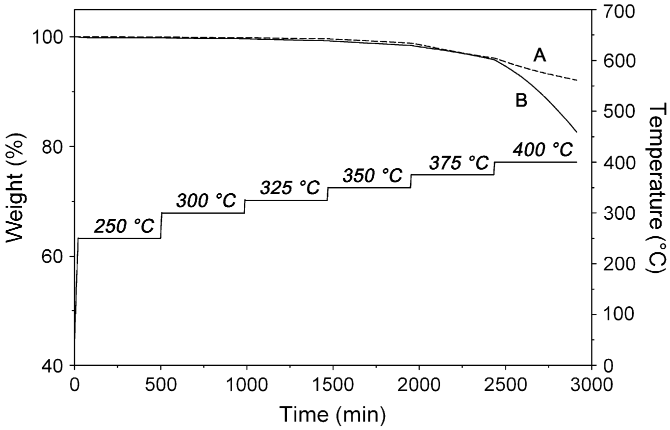


Fig. 6. Oxidative aging of polymers **6a** (A) and **7a** (B) heated from 250 to 400 °C in 8 h temperature segments after being cured with 3% *p*-BAPS to a maximum temperature of 375 °C.

were seen over the same temperature range. Moreover, when resins **6a** and **6b** were heated further at 400 °C for 8 h, additional weight losses of 4 and 6.6% were observed. These results were superior and represented a significant improvement in the oxidative stability relative to **7a** and **7b** whereby weight losses of around 2–3 times that of **6a** and **6b** were noted at 400 °C over the same period of time.

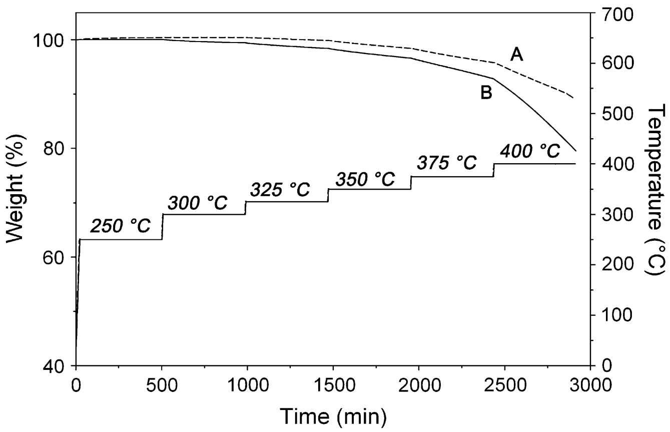
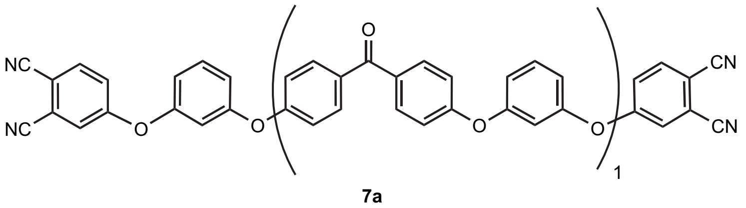


Fig. 7. Oxidative aging of polymers **6b** (A) and **7b** (B) heated from 250 to 400 °C in 8 h temperature segments after being cured with 3% *p*-BAPS to a maximum temperature of 375 °C.

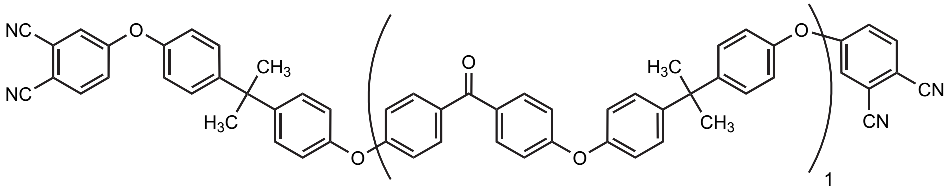
Table 1
Oxidative aging data for polymers **6** and **7** heated from 250 to 400 °C in 8 h temperature segments under air

Temperature (°C)	Total weight loss (**6a**) (%)	Total weight loss (**7a**) (%)	Total weight loss (**6b**) (%)	Total weight loss (**7b**) (%)
250	0.0	0.0	−0.4	−0.1
300	0.1	0.1	−0.4	0.5
325	0.3	0.5	0.3	1.6
350	1.1	1.3	1.7	3.3
375	3.9	4.0	4.2	7.2
400	7.9	17.1	10.8	20.4

Scanning electron microscopy (SEM) studies were performed on samples of **6** to assess the damage caused by long-term oxidative aging up to high temperatures. Fig. 9 shows images of resin **6b** before and after heating in an air flow from 250 to 400 °C in 8 h temperature segments. A cracked layer, which was measured using the SEM software



7a



7b

Fig. 8. Structure of previously developed oligomeric phthalonitrile resins **7a** and **7b**.

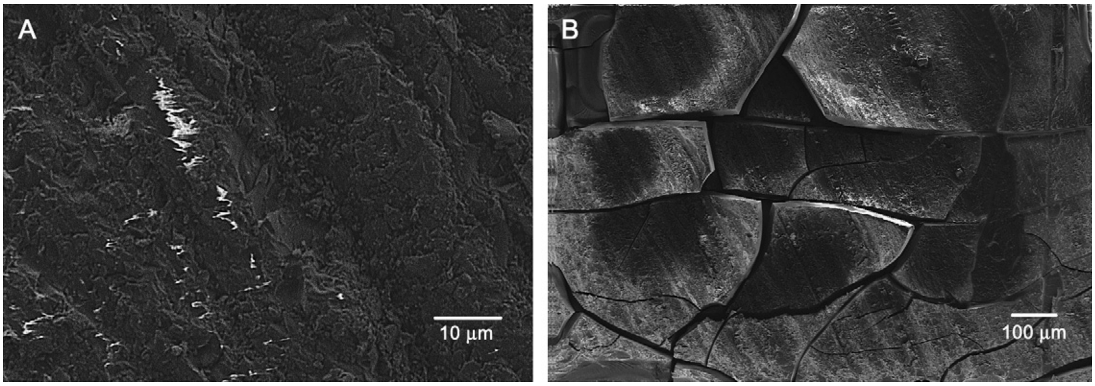


Fig. 9. SEM images of resin **6b**: before (A) and after (B) long-term oxidative aging.

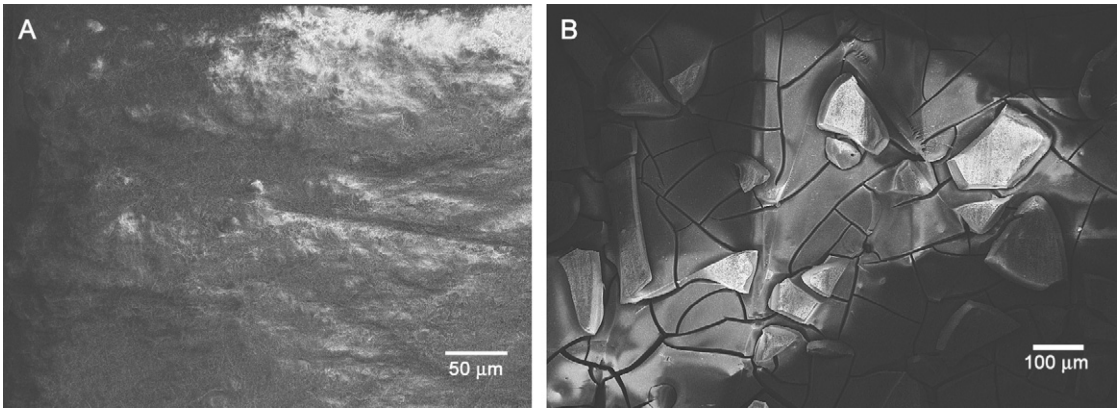


Fig. 10. SEM images of resin **7b**: before (A) and after (B) long-term oxidative aging.

to be approximately 15 μm thick, was present on both sides of the oxidized sample (Fig. 9B). Similar images were obtained for a sample of **7b**, which showed more extensive damage with cracked outer layers approximately 25 μm thick (Fig. 10) as measured from the SEM software. More damage appeared on the surface of **7b** and appeared to occur to a greater depth relative to **6b**. This observation indicated that the phosphorus enhanced the oxidative protection of **6**.

4. Conclusion

The described synthetic scheme provides a two-step method for the formation of a multiple aromatic ether-linked phosphine oxide containing phthalonitrile **1** with a flexible spacer between the reactive end groups. The monomer **1** exhibits an amorphous softening temperature at around 75–90 °C and is completely free flowing at around 150 °C. Polymerization to a thermoset does not occur until the composition (**1** and *p*-BAPS) is heated above 230 °C. Polymer **6** does not exhibit a T_g when fully cured and maintains structural integrity at elevated temperatures. When polymer **6** was compared to a non-phosphorus containing phthalonitrile resin **7** of similar structure, a notable improvement in the long-term oxidative stability was also observed. The combination of these properties makes these polymers good candidates in the fabrication of structural composite components for advanced aerospace applications.

Acknowledgements

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