Imide-containing phthalonitrile resin

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A new imide-containing phthalonitrile resin has been synthesized and studied by thermal analysis. The initially formed di(amic acid) phthalonitrile intermediate, which was synthesized from reaction of 4-(3-aminophenoxy)phthalonitrile with 3,3′,4,4′-benzophenonetetracarboxylic dianhydride, is readily converted into the imide linkages before commencing with the polymerization reaction. The monomer was polymerized in the presence of a minute quantity of 1,3-bis(3-aminophenoxy)benzene by an addition polymerization reaction. Thermal properties were determined by differential scanning calorimetry and thermogravimetric analysis.

(Keywords: phthalonitrile; imide; thermal stability; oxidative stability; glass transition temperature; addition reaction)

INTRODUCTION

Polyimides have received considerable attention as composite matrices and are being investigated as dielectric materials for microelectronic applications because of their thermal and thermo-oxidative stability. Conventional high temperature polyimides are synthesized in two steps from reaction of an aromatic dianhydride with an aromatic diamine in a dipolar aprotic solvent[1]. The initially formed high molecular weight poly(amic acid) intermediate, being soluble in numerous solvents, is used for product fabrication. Further reaction or curing of this intermediate by either thermal or chemical means results in the formation of imide linkages. Such polyimides are difficult to fabricate into finished products because of insolubility problems associated with the high aromatic character of the polymeric backbone. During the imidization reaction, the evolution of volatile by-products leads to the formation of voids in the finished product. The presence of these voids is very undesirable because of their effect on the mechanical properties. To minimize void formation in composites, the polymerization reactions are performed under pressure to hold the volatiles inside the resin until after gelation occurs.

The void problem can be solved by the development of fully imidized monomers or prepolymers, which are encapped with reactive end groups for polymerization purposes[2–7]. This approach entails the incorporation of imide linkages between terminal groups that are capable of polymerizing and forming crosslinked polymers. The volatile by-product formed from the imidization reaction is eliminated before commencing with the polymerization reaction. Polymerization occurs by addition-type reactions yielding void-free polymeric materials.

Phthalonitrile-based polymers constitute a class of high temperature materials having a wide range of potential uses such as composites matrices[8] and electrical conductors[9–11]. Polymerization takes place through the cyano groups by an addition mechanism to afford heterocyclic crosslinked products, which are known to exhibit good thermal and oxidative stability. Previous work in this laboratory on high temperature polymers has mainly dealt with highly aromatic, diether-linked phthalonitriles[12–18]. The monomers were prepared by the nucleophilic displacement of a nitro group from 4-nitrophthalonitrile by the dialkali salts of bisphenol-based compounds. Only a minute quantity of curing additive is needed to initiate the polymerization reaction. The polymerization rate can be easily controlled as a function of the concentration of curing additive and curing temperature. The polymerization reaction can be performed in one step by heating the melt of the phthalonitrile–amine mixture until gelation occurs. Alternatively, the polymerization mixture can be advanced to any viscosity desired (B-staged) and quenched. The B-staged prepolymer is stable indefinitely under ambient conditions. The stability of the prepolymer at ambient temperatures is particularly attractive for the preparation of prepregs and their applications as laminates for fibre-reinforced composites. As a further extension of this work, interconnecting units containing both aromatic ether and imide linkages have been incorporated between the terminal phthalonitriles[2]. The polymerization reaction was performed in the presence of a thermally stable aromatic diamine[14–18]. This paper is concerned with the synthesis and polymerization of an imide-containing phthalonitrile and its characterization by thermal and oxidative means.

EXPERIMENTAL

Thermal analyses were performed with a DuPont 1090 thermal analysis system equipped with a thermogravimetric analyser (t.g.a., heating rate 10°C min^{-1}) and a differential scanning calorimeter (d.s.c., heating rate 10°C min^{-1}). The thermal and oxidative stabilities were determined between 25°C and 800°C in air and nitrogen atmospheres at a flow rate of 50 cm^3 min^{-1}. The glass transition temperature (T_g) was reported as the temperature centred at the midpoint between the linear baselines

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of a d.s.c. scan. Dimethyl sulfoxide (DMSO) was dried by distillation over calcium hydride. Dimethylformamide (DMF) was dried over molecular sieves. The 3-aminophenol and 3,3',4,4'-benzophenonetetracarboxylic anhydride were obtained from Aldrich and used as received without further purification. The 4-nitrophthalonitrile was acquired from Eastman Kodak. The chemical reactions were monitored using a Perkin Elmer 1800 *FT*i.r. spectrophotometer.

Synthesis of 4-(3-aminophenoxy)phthalonitrile 1

A mixture containing 3-aminophenol **2** (20.1 g, 184.4 mmol), 50% aqueous sodium hydroxide (7.4 g, 185.0 mmol), and 150 ml DMSO was placed in a 300 ml flask fitted with a Dean–Stark trap. The resulting mixture was purged with nitrogen and heated at 90°C for 1 h. To the solution was added 30 ml toluene. The solution was then heated to reflux and the water was removed azeotropically over a period of 4 h. The reaction was monitored by *FT*i.r. spectroscopy by observing the disappearance of the nitro absorptions at 1540 and 1358 cm^{-1}. After removing the toluene by distillation, 4-nitrophthalonitrile **3** (31.9 g, 184.4 mmol) was added to the reaction mixture followed by stirring at room temperature for 4 h and at 60°C for 4 h. After cooling, the resulting dark mixture was poured into 300 ml of cold, dilute hydrochloric acid. The crude dark brown solid which separated was collected by suction filtration, washed with water until neutral, and dried. Recrystallization from toluene under nitrogen using activated charcoal afforded 34.5 g (80%) of **1**, m.p. 171–173°C, reported[19] m.p. 172–173°C.

Synthesis of imide-containing phthalonitrile 5

To a 100 ml, three-necked flask was added 3,3',4,4'-benzophenonetetracarboxylic dianhydride (BTDA) **4** (5.4 g, 16.7 mmol) and 30 ml dry DMF. After flushing the solution with nitrogen for 20 min, 4-(3-aminophenoxy)-phthalonitrile **1** (7.8 g, 33.3 mmol) was added under ambient conditions. The temperature of the reaction mixture was increased to 90°C and held at this temperature for 1 h. Toluene (30 ml) was added and the solution was heated to reflux. The water, which was formed as a by-product, was removed azeotropically from the mixture with a Dean–Stark trap. Total reflux time was 12 h. After removing the toluene by distillation and cooling, the white solidified product mixture was removed from the reaction vessel, washed with ethanol, collected by filtration, dried, and heated at 200°C for 2 h to afford 11.9 g (93%) of **5**, m.p. 245–248°C.

Polymerization of phthalonitrile 5

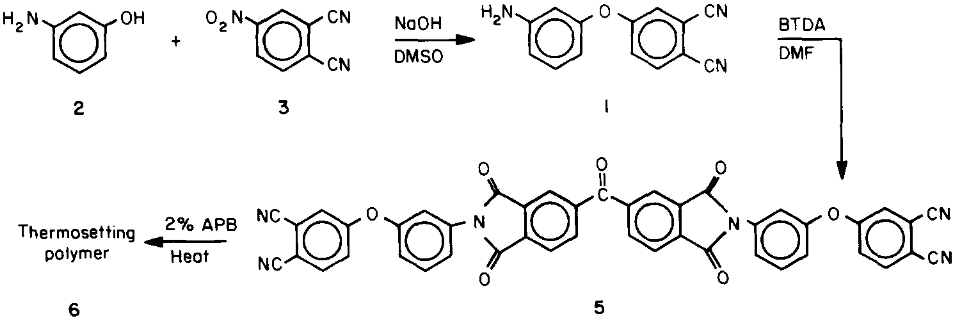
To the melt of **5**, which had been degassed for 5 h at reduced pressure, was added 1,3-bis(3-aminophenoxy)-benzene (APB, 2 wt%) with stirring. The resulting dark polymerization mixture was cured by heating at 210–300°C for 5–18 h and at 316°C for 16 h. The polymer **6** was post-cured at temperatures up to 375°C to optimize physical properties. When exposed to temperatures in excess of 316°C, **6** was post-cured under an inert atmosphere.

RESULTS AND DISCUSSION

The synthesis of the imide-containing phthalonitrile **5** involves a displacement reaction to prepare the ether linkage and a condensation reaction to form the imide ring. Initially, 4-(3-aminophenoxy)phthalonitrile **1** was synthesized by the nucleophilic displacement of a nitro substituent from 4-nitrophthalonitrile **3** by the sodium salt of 3-aminophenol **2** in dry DMSO under an inert atmosphere[19]. Compound **1** was stable and did not form a homopolymer under the reaction conditions. Toluene was used as an azeotropic solvent to remove the water formed as a by-product and to control the reaction temperature. Further reaction of **1** with BTDA **4** in DMF resulted in the initial formation of a di(amic acid) intermediate terminated with phthalonitrile units. Conversion of the amic acid moieties into imide linkages was accomplished under refluxing conditions using toluene as azeotropic solvent. In some cases, complete imidization had not occurred after 12 h of reaction time, as determined by a broad melting point range for **5**. Such samples were heated at 200°C for a short time to thermally complete the imidization reaction (*Scheme 1*).

Thermal analysis studies on **5** provided information concerning the conditions necessary for its polymerization. A t.g.a. thermogram at 25–375°C did not show any loss of weight. A d.s.c. thermogram (*Figure 1*) showed transitions peaking at 134 and 142°C (weak, endothermic, amorphous), at 179°C (moderate, exothermic, crystallization) and at 246°C (strong, endothermic, melting point). When the sample was quickly cooled to room temperature and the d.s.c. thermogram repeated, only one transition was observed, centred at 125°C and indicative of a phase transition from a glassy state. The initial endothermic and exothermic transitions attributed to phase transitions at 134 and 142°C and at 179°C, respectively, were now missing. Moreover, since **5** does not readily recrystallize from the melt, polymerization can be achieved at considerably lower temperatures than the initial melting point and at a temperature above the T_g of the glassy state.

Completely imidized phthalonitrile **5** can be readily polymerized from the melt in the presence of an aromatic amine. Samples of **5** were initially heated at 250–260°C



Scheme 1

and degassed at reduced pressure to remove residual solvent. The temperature of the melt was then reduced and APB was added above the T_g (125°C). The viscosity was fairly high near this transition. Thus, it was best to add the amine curing agent (APB) at a higher temperature where homogeneous mixing could be readily performed. For this study, 2 wt% of APB was added at approximately 210°C. These results showed that the processing conditions, especially the cure time and temperature, can be controlled as a function of the concentration of **5** and APB. Moreover, when carried out under the same polymerization conditions, larger ratios of APB to **5** resulted in a shorter reaction time to gelation. The time to gelation can be easily controlled as a function of the amine concentration (APB) and reaction temperature.

The **5**–APB polymerization reaction was studied by d.s.c. analysis (*Figure 2*). After heating **5** above its melting point and cooling to approximately 210°C, APB (2 wt%) was added with stirring to the melt. Upon quickly quenching to room temperature and testing, the sample exhibited a T_g of 125°C (curve A). The d.s.c. thermogram did not show an exothermic reaction from the initial reaction of the APB with **5**. This reaction had already occurred. Further heating of the sample at 210°C resulted in an enhancement in viscosity indicative of prepolymer formation. After heating the sample for 30 min at 210°C, a d.s.c. thermogram showed an increase in the T_g to 135°C (curve B). Additional heating at 260°C for 5 h resulted in a shift of the T_g to 210°C (curve C). When a d.s.c. scan (25–350°C) was obtained of a sample that had been cured by heating at 210°C for 4 h, at 260°C for 8 h, and at 316°C for 16 h, a distinctive viscoelastic transition from the glassy state to the rubbery state was not observed. Apparently, the crosslinking density had increased to a point where little molecular mobility was present within the polymeric backbone.

Figure 3 shows t.g.a. thermograms of **6** in nitrogen. The polymeric stability was found to be a function of the curing cycle and post-cure temperatures. The thermal stabilities were determined on samples that had been cured at 210°C for 4 h, at 260°C for 8 h, and at 316°C for 16 h and post-cured at 350°C for 4 h and at 375°C for 4, 12 and 24 h, respectively. As the temperature exposure was increased from 316 to 350°C (curves A and B), an improvement in the thermal stability was observed. Further heating of **6** to 375°C showed a less pronounced progression in the thermal properties (curves C and D). All samples post-cured at 375°C for various times showed the same stability.

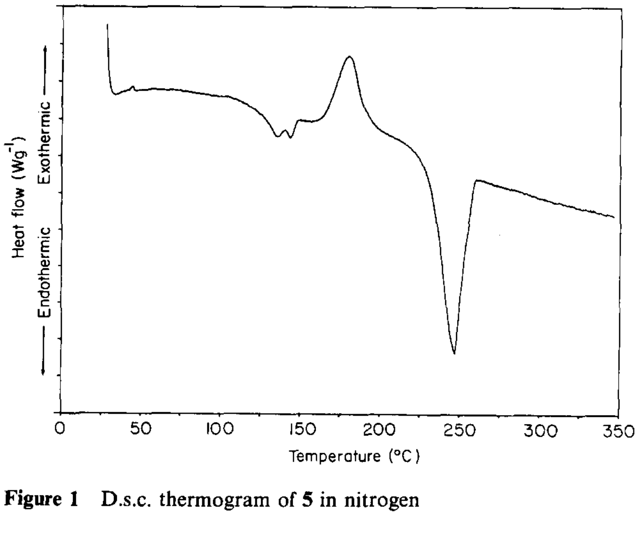


Figure 1 D.s.c. thermogram of **5** in nitrogen

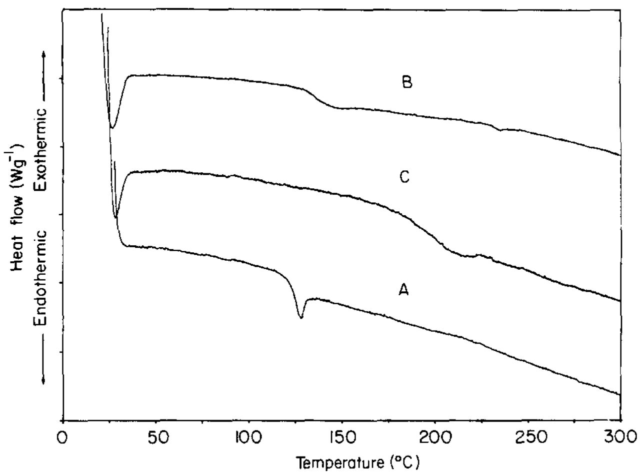


Figure 2 Polymerization study of **5** by d.s.c. analysis: A, addition of APB (2 wt%) to melt at 210°C, and cooled to room temperature; B, isotherm at 220°C for 30 min after addition of amine additive; C, isotherm at 260°C for 5 h after addition of amine additive

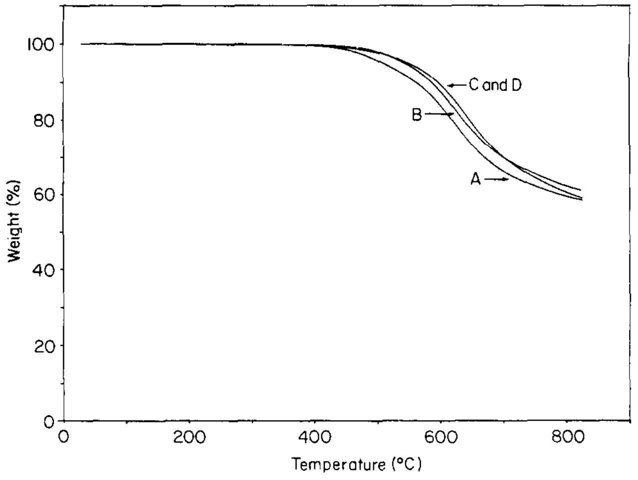


Figure 3 T.g.a. thermogram of powdered **6** in nitrogen after heat treatment in sequence at: A, 210°C for 4 h, 260°C for 8 h, and 316°C for 16 h; B, 350°C for 4 h; C, 375°C for 4 h; D, 375°C for 24 h

Figure 4 shows the oxidative stability of **6** in air. Samples of **6** were tested that had been cured by heating at 210°C for 4 h, at 260°C for 8 h, and at 316°C for 16 h and post-cured at 350°C for 4 h and at 375°C for 12 and 24 h. Samples cured at a maximum temperature of 316°C and then post-cured at 350°C showed similar stabilities with catastrophic degradation occurring above 550°C (curves A and B). Further treatment of **6** at 375°C resulted in a reduction in the oxidative stability (curves C and D).

The thermal studies show that the overall thermal and oxidative stabilities are dependent on the temperature exposure that **6** sees. The reduction in oxidative stability as **6** is heated at elevated temperatures is probably associated with a breakdown in the linking structure connecting the terminal phthalonitrile units. These observations indicate that thermal breakdown resulting in the degradation of bond and the ultimate reaction of free radicals with oxygen becomes more prevalent when **6** is exposed to temperatures in excess of 350°C.

When compared to other phthalonitrile resins containing aromatic ether functional moieties within the linking units, **6** did not exhibit the expected oxidative stability at elevated temperatures. For the bisphenol-based phthalonitrile resins[8,18], the thermo-oxidative stability was enhanced as the post-cured temperature was increased from 350 to 375°C, which was in contrast to the situation observed for **6**. However, the imide-linked phthalonitrile **6** was more oxidatively stable in that catastrophic decomposition occurred at a higher temperature than the bisphenol-based phthalonitrile resins, e.g. 4,4′-bis(3,4-dicyanophenoxy)biphenyl, when processed under identical thermal conditions (*Figures 5* and *6*). Since **6** contains both ether and imide linkages, these findings probably indicate that the initial breakdown within the polymeric backbone occurs at the imide moiety.

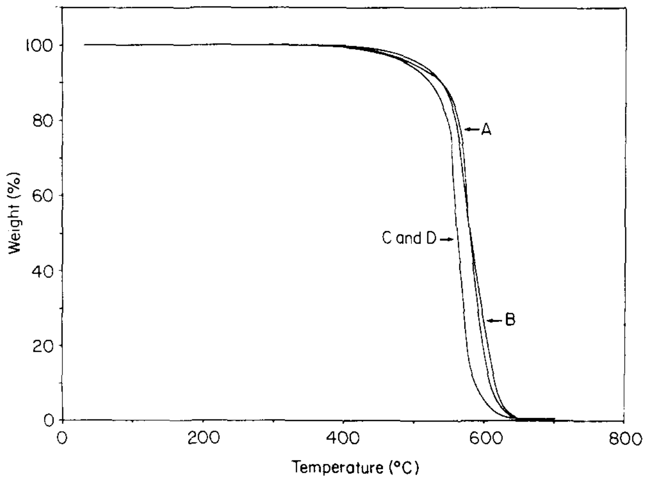


Figure 4 T.g.a. thermogram of powdered **6** in air after heat treatment in sequence at: A, 210°C for 4 h, 260°C for 8 h, and 316°C for 16 h; B, 350°C for 4 h; C, 375°C for 12 h; D, 375°C for 24 h

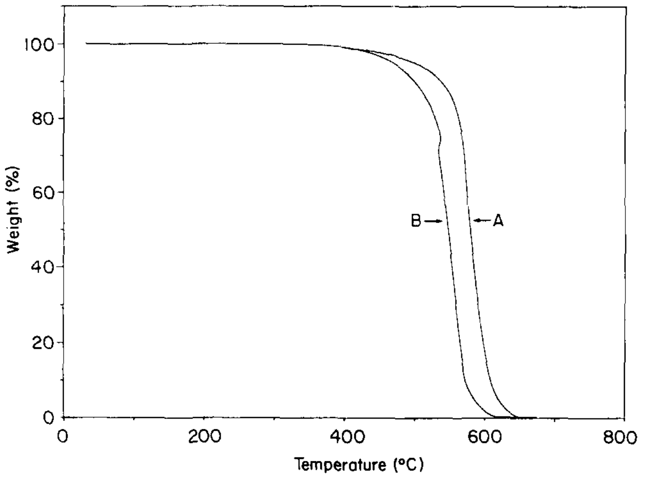


Figure 5 Comparative t.g.a. thermogram of powdered phthalonitrile resins in air after heat treatment at 210°C for 4 h, at 260°C for 8 h, and at 316°C for 16 h: A, polymer **6**; B, 4,4′-bis(3,4-dicyanophenoxy)biphenyl

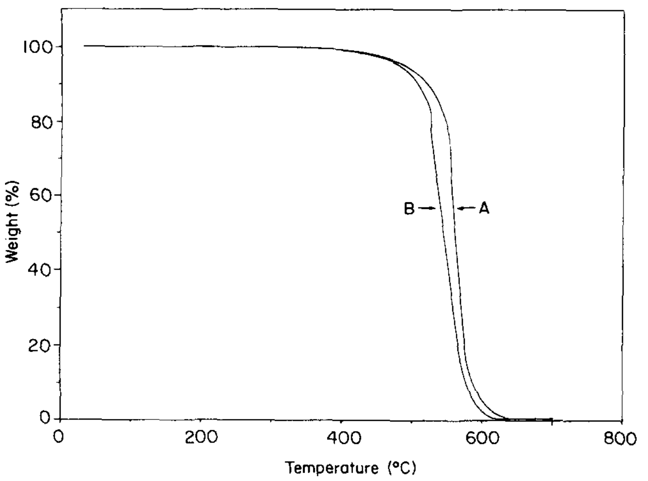


Figure 6 Comparative t.g.a. thermogram of powdered phthalonitrile resins in air after heat treatment at 210°C for 4 h, at 260°C for 8 h, and at 316°C for 16 h and post-curing in sequence at 350°C for 4 h and at 375°C for 12 h: A, polymer **6**; B, 4,4′-bis(3,4-dicyanophenoxy)biphenyl

CONCLUSION

The imide-linked phthalonitrile **6** shows good thermal and oxidative stability. The synthesis is short and occurs in high yield. Since the imide linkages in the interconnecting unit between the terminal phthalonitriles are formed before polymerization occurs, void-free components can be fabricated. Once melting occurs and the degassed monomer is converted into the amorphous phase, the polymerization reaction can be carried out below the melting point but at a temperature above the softening point (T_g) of the glassy form. Polymer **6** shows superior oxidative stability relative to the bisphenol-based polymers when cured under identical conditions. An enhancement in the thermal stability was observed as the sample was exposed to elevated temperatures. However, a reduction in oxidative stability was noted when **6** was exposed to temperatures above 350°C.

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