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High temperature resorcinol-based phthalonitrile polymer

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Abstract

Resorcinol-based phthalonitrile, 1,3-bis(3,4-dicyanophenoxy)benzene, has been synthesized in high yield by a simple nucleophilic displacement of a nitro-substituent from 4-nitrophthalonitrile in a dipolar aprotic solvent. The monomer can be thermally polymerized to a network polymer in the presence of an amine curing additive. The resin is readily processed in a controlled manner as a function of temperature and quantity of additive. Thermal analyses and rheology studies were used to characterize the high temperature thermosetting phthalonitrile polymer.
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1. Introduction

During the past 30 years considerable research efforts have been expended on the development of high temperature polymers for aerospace applications. Until recently, most high temperature composite materials were based on polyimides, which have been mainly fabricated by pre-preg consolidation. Polyimides with aromatic units in the backbone have been mainly used for structural aerospace applications where durability at temperatures as high as 200–300 °C is needed. Linear polyimides [1] are extremely tedious to process, are insoluble in solvents, and liberate volatile by-products such as water during the imidizing polymerization reaction producing void-filled fabricated components.

Efforts to solve the void problem in polyimides have centered on the development of cross-linked or networked systems, which are formed from low molecular weight imide-containing pre-polymers endcapped with unsaturated groups (double or triple bonds) [2–4]. Although the imide pre-polymers have substantially solved the void problems, other issues such as high viscosity and/or high processing temperatures have kept these resins from being fully utilized

for broad high temperature applications. The PMR-resin systems terminated by nadic groups exhibit high viscosity at the processing temperature and must be stored at low temperatures to impede the polymerization reaction. Polymerization in the nadic group occurs through a carbon–carbon double bond and the resulting aliphatic cross-linking centers are weak sites for thermo-oxidative degradation [5], which limits their usage for high temperature applications. The oligomeric phenylethynyl-terminated polyimides have a large processing window and are heated at or above 350 °C to thermally initiate the polymerization reaction through the phenylethynyl groups [6,7].

Research efforts at the Naval Research Laboratory have been concerned with the development of thermosetting phthalonitriles for potential aerospace, marine, and electronic packaging applications at temperatures up to 375 °C (700 °F). The addition cure mechanism of these systems ensures that little or no volatiles are evolved during the polymerization leading to highly cross-linked, void-free network polymers having good mechanical properties, outstanding thermo-oxidative stability at elevated temperatures, superior fire resistance relative to other conventional polymers, and low water absorptivity. The advanced composite materials based on the phthalonitriles have now reached a level of maturity that makes them a viable structural material. The phthalonitrile monomers are commercially available. Glass and carbon fiber-reinforced composites are being evaluated for numerous domestic and military applications. The fire performance of phthalonitrile

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composites is superior to that of other thermoset-based composites currently being evaluated for aerospace, ship, and submarine applications.

Phthalonitrile-based monomers have previously been synthesized and polymerized with aromatic ether [8–13], thioether [14], imide [15,16], and sulfone [17,18] linkages incorporated between the terminal phthalonitrile units. To date, most of our research efforts have evolved around the reaction of aromatic amines such as 1,3-bis(3-aminophenoxy)benzene (*m*-APB) or bis[4(4-aminophenoxy)phenyl]sulfone (*p*-BAPS) with 4,4′-bis(3,4-dicyanophenoxy)biphenyl to produce a highly cross-linked polymerization system. Pure 4,4′-bis(3,4-dicyanophenoxy)biphenyl melts at 233–234 °C and immediately reacts with aromatic amine curing additives [19]. Thus, the phthalonitrile–amine composition exhibits a small processing window ($\sim$20 °C) defined as the temperature difference between the melting point of the phthalonitrile and the exothermic curing temperature. Thermogravimetric studies show that the polymers of 4,4′-bis(3,4-dicyanophenoxy)biphenyl commence to slowly lose weight at about 450 °C upon heating at 10 °C/min in an inert atmosphere with catastrophic weight loss occurring between 500 and 550 °C. Glass and carbon fiber-reinforced phthalonitrile composites [20–22] fabricated from 4,4′-bis(3,4-dicyanophenoxy)biphenyl meet the Navy specification (MIL-STD-2031) for usage of a polymeric composite on the interior of a submarine. Beside the unique physical properties exhibited by the phthalonitrile network polymers, broad interest in these systems centers on the control of the viscosity as a function of the curing additive and reaction time and the ease of processability by advanced composite fabrication techniques. Due to the high melting points of the phthalonitrile monomers, only catalytic amounts of curing additives can be used for the polymerization reaction.

Our current research effort in high temperature phthalonitrile resins is concerned with the development of new monomers, which have lower melting points, can be polymerized at moderately elevated temperatures, and yield highly cross-linked thermally stable systems suitable as matrices for long-term, high temperature composite applications up to 343 °C (650 °F). The development of phthalonitrile-based monomers that have a large processing window between the melting point and the initiation of polymerization is being pursued. Such materials are important in the fabrication of polymeric composites by more cost-effective processing methods such as resin transfer molding (RTM), resin infusion molding, and vacuum-assisted resin transfer molding (VARTM), computerized filament winding, etc. Replacement of metals by such polymeric composites can affect substantial weight and energy savings and improve their performance characteristics. This paper is concerned with the synthesis and polymerization of resorcinol-based phthalonitrile **1**, 1,3-bis(3,4-dicyanophenoxy)benzene, which has a larger processing window relative to previous phthalonitrile

monomers. Thermal and mechanical characterization of **1** will also be presented.

2. Experimental

Thermal analysis was performed on powdered and film samples using a TA Instruments Q50 thermogravimetric analyzer (TGA) and a 2920 differential scanning calorimetry (DSC) at a heating rate of 10 °C min^{-1}. The thermal and oxidative stabilities were determined between 25 and 1000 °C in air and nitrogen and air, respectively, at a flow rate of 100 cc/min. Dimethyl sulphoxide (DMSO) was dried over calcium hydride before distillation at reduced pressure. The 4-nitrophthalonitrile was acquired from Eastman Kodak. 1,3-Bis(3-aminophenoxy)benzene (*m*-APB) and bis[4(4-aminophenoxy)phenyl]sulfone (*p*-BAPS) were used as received from Mitsui Toatsu Chemicals, Inc. and Chriskev Company, Inc., respectively. The chemical reactions were monitored using a Perkin Elmer 1800 FT-IR spectrophotometer. Mechanical studies were performed on a TA Instruments AR-2000 rheometer in conjunction with an environmental testing chamber for temperature control.

2.1. Synthesis of 1,3-bis(3,4-dicyanophenoxy)benzene 1

To a 200 ml, three-necked flask was added resorcinol **2** (5.51 g, 0.050 mol), 4-nitrophthalonitrile **3** (17.33 g, 0.10 mol), and pulverized anhydrous potassium carbonate (20.81 g, 0.15 mol), and 60 ml of dry DMSO. During the course of the reaction, the potassium carbonate was added in three portions. While stirring, the resulting mixture was heated at 80–90 °C for 5 h under an inert atmosphere. After cooling, the product mixture was poured into 300 ml of dilute HCl solution. The off-white solid **1** (14.9 g, 82% yield) was collected by suction filtration and washed with water until the filtrate was neutral. A small amount of **1** was recrystallized from acetonitrile for analytical purposes, mp 183–185 °C. $C_{22}H_{10}N_4O_2$ (362.22): calcd C 72.94, H 2.76, N 15.46 O 8.83; found C 72.74, H 2.76, N 15.34, O 9.16.

2.2. DSC studies on 1 and curing additive

Cure studies were performed on **1** by DSC analysis using various amounts (2.4 and 5.8 mol%) of *m*-APB and *p*-BAPS. The compositions were thoroughly mixed in powdered form under ambient conditions. Samples were then evaluated from room temperature to 400 °C under a nitrogen atmosphere.

2.3. TGA studies on 4

The thermal and oxidative properties were obtained using TGA analyses on films of **4** prepared in a TGA chamber by heating **1** and various amounts (2.4 and

5.8 mol%) of *m*-APB and *p*-BAPS at 250 °C for 2 h, 325 °C for 2 h, 350 °C for 4 h, and 375 °C for 8 h under a flow of nitrogen. Measurements up to 1000 °C were made in nitrogen and air atmospheres, respectively.

2.4. Rheometric studies on 4

The storage modulus and loss factor curves were obtained on samples of **4** containing 2.4 mol% of *m*-APB and *p*-BAPS in nitrogen over the temperature range of ~40–500 °C. Rectangular samples (45×12×2 mm) of **4** were fabricated by heating **1** and the amine additive in an argon atmosphere at 250 °C for 2 h, 325 °C for 2 h, 350 °C for 4 h, and 375 °C for 8 h. An oscillatory temperature ramp of 3 °C min⁻¹ was used to determine the modulus at a frequency of 1 Hz and a strain of 2.5×10^{-4}%. Normal force control was utilized throughout the tests to keep the samples taut.

3. Results and discussion

Resorcinol-based phthalonitrile monomer **1** (Scheme 1) is synthesized in high yield by a simple nucleophilic displacement of a labile nitro-substituent from 4-nitrophthalonitrile **3** by the dialkaline salt of resorcinol **2**. The reaction takes place in a dry dipolar aprotic solvent, e.g. DMSO and DMAC, and in the presence of either weak or strong bases [9]. The use of a dry solvent permits the monitoring of the amount of water that formed and the determination of when the reaction is completed. Bases that can be used include sodium carbonate, potassium carbonate, sodium hydroxide, and potassium hydroxide. When using a strong base such as sodium hydroxide or potassium hydroxide, the water, formed as a by-product during the formation of the dialkaline salt of **2**, is removed by azeotropic distillation
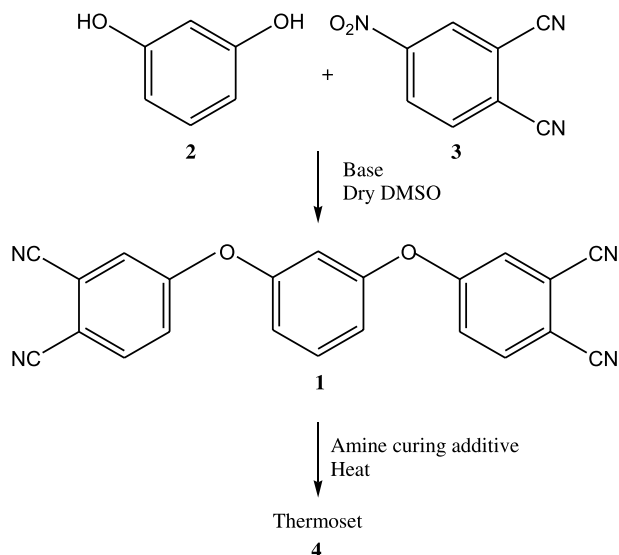
Scheme 1. Synthesis and polymerization of **1**.

before the addition of **3** to prevent reaction with the cyano substituents.

The reaction of **1** with 2.4 and 5.8 mol% of *m*-APB and *p*-BAPS was studied by DSC analysis. Pure **1** has a melting point of 185 °C. To obtain homogeneous mixtures, **1** and the curing additive were thoroughly mixed by stirring. Characteristic melting peaks in the mixtures were observed for the curing additives, *m*-APB and *p*-BAPS, and **1** peaking at 105–106 and 163 °C and at 173–179 °C, respectively. Exotherms peaking at about 267 and 269 °C and at about 252 and 258 °C for 2.4 and 5.8 mol% of *m*-APB and *p*-BAPS, respectively, are attributed to their reaction with **1**. Fig. 1 shows the DSC thermograms for **1** and 2.4 mol% of *m*-APB and *p*-BAPS heated to 400 °C. These results show a large processing window (~70–100 °C) between the melting point of **1** and the polymerization temperature. Thus, larger amounts of curing additive, which would be expected to affect the physical properties of the cured phthalonitrile polymers, can be used. For the fabrication of thick composite components by RTM and resin infusion molding, the viscosity of the curing mixture can be readily controlled as a function of the temperature and the quantity of curing additive.

The phthalonitrile monomer **1** is easily processed into a shaped component in a controlled manner. After the addition of *m*-APB or *p*-BAPS to the melt of **1**, the reaction mixture is rapidly converted from a crystalline into an amorphous phase (pre-polymer). Moreover, the polymerization reaction can be performed in one step to gelation or can be advanced to any viscosity desired (B-staged pre-polymer), quenched, and stored at room temperature until ready to convert into a thermosetting material or used in the fabrication of a composite component. The B-staged pre-polymer is stable indefinitely under ambient conditions and is soluble in numerous common organic solvents such as methylene chloride, chloroform, and the dipolar aprotic solvents. When ready, the curing of a mixture containing **1** and the amine additive can be completed by raising the temperature to or above the polymerization reaction temperature.

The thermal stability of thermosetting phthalonitrile polymers **4** that had been cured in the presence of various molar amounts of *m*-APB or *p*-BAPS was determined by TGA analysis in an inert atmosphere. The samples cured with 2.4 mol% of *m*-APB and *p*-BAPS showed char yields of 70 and 66%, respectively, when heated to 1000 °C (Fig. 2). A study of pure **1** showed that the monomer commenced to slowly lose weight at about 300 °C with catastrophic weight loss occurring between 350 and 440 °C. Thus, high conversion to the thermoset or network is important in the initial cure at 250 °C. The *m*-APB cured sample showed a slightly higher weight retention at 1000 °C, which was attributed to the enhanced reactivity relative to *p*-BAPS [19]. Samples containing 5.8 mol% of *m*-APB and *p*-BAPS exhibited similar thermal properties with a weight retention of about 74
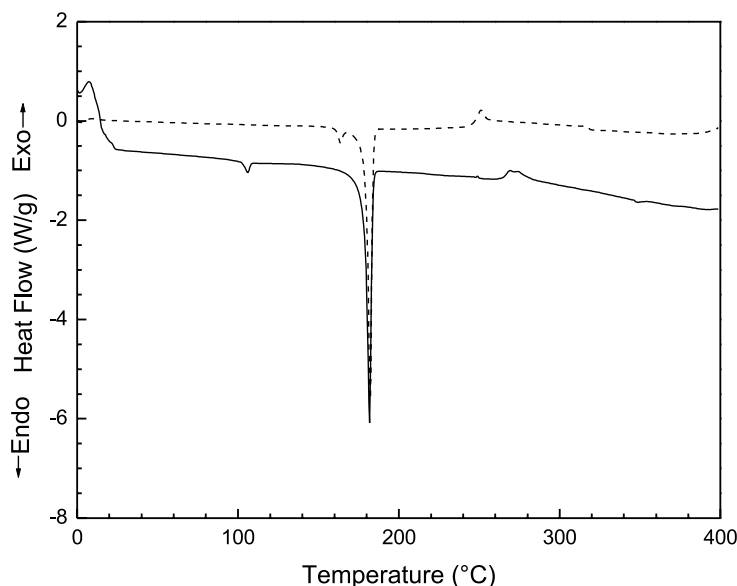
Fig. 1. DSC thermograms of **1** in the presence of 2.4 mol% of *m*-APB (solid line) and *p*-BAPS (dash line).

and 73%, respectively. The smaller weight losses for the larger amounts of curing additive is probably attributed to enhancement in the cure reaction resulting in a reduction in the availability of unreacted **1** for volatilization. The curing and thermal exposure results indicate that the thermal stability is a function of the amount of amine curing additive used in the polymerization reaction.

The thermo-oxidative properties for **4** were determined on films, obtained from a **1** and 2.4 mol% of *m*-APB and *p*-BAPS, cured to a maximum temperature of 375 °C for 8 h (Fig. 3). Both samples showed similar oxidative stability to about 450 °C with catastrophic decomposition occurring between 500 and 700 °C. Above 500 °C, the thermal and oxidative degradation process for the *p*-BAPS cured sample commenced at a higher temperature relative to the *m*-APB cured film.

The storage modulus, G', and the loss factor, tan δ, of **4**, cured in the presence of 2.4 mol% of *m*-APB and *p*-BAPS to a maximum temperature of 375 °C for 8 h, were evaluated between 40 and 500 °C in a nitrogen atmosphere using a rheometer in the torsional mode. Fig. 4 compares the storage modulus and the loss factor curves of the polymers cured with the two amine additives under identical conditions. At 40 °C, the moduli of the samples were about 1 GPa. With temperature increases up to 400 °C, the samples exhibited only a gradual decrease in the storage moduli and a small increase in tan δ above 375 °C. This is evidence that the polymers retained very good mechanical properties at elevated temperatures. Above 375 °C, the modulus for the *m*-APB cured sample commenced to slowly decline and the tan δ values started to rise indicating a slight softening of the sample and further cure. The *p*-BAPS cured sample
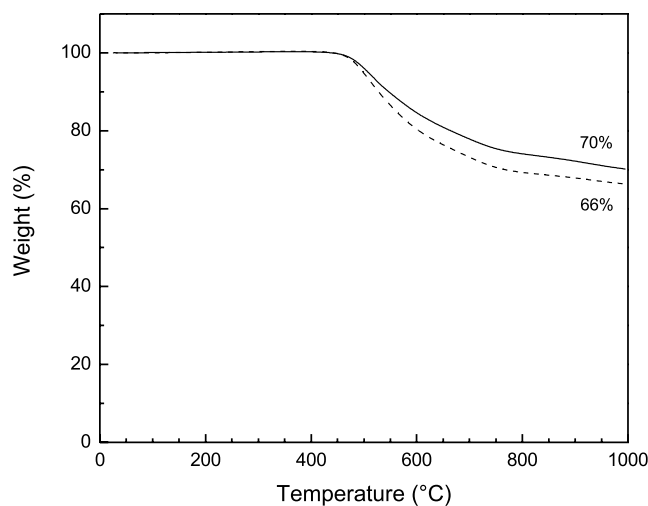

Fig. 2. Thermal stability of **4** cured with 2.4 mol% of *m*-APB (solid line) and *p*-BAPS (dash line) and heated to 1000 °C in a flow of nitrogen.
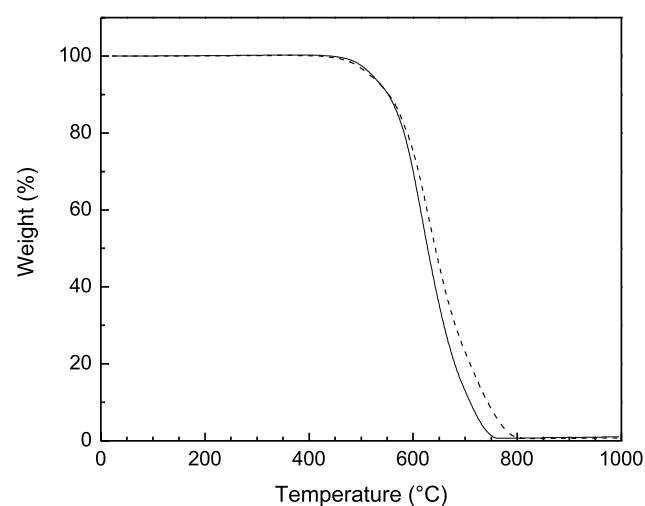

Fig. 3. Thermo-oxidative stability of **4** cured with 2.4 mol% of *m*-APB (solid line) and *p*-BAPS (dash line) and heated to 1000 °C in a flow of air.
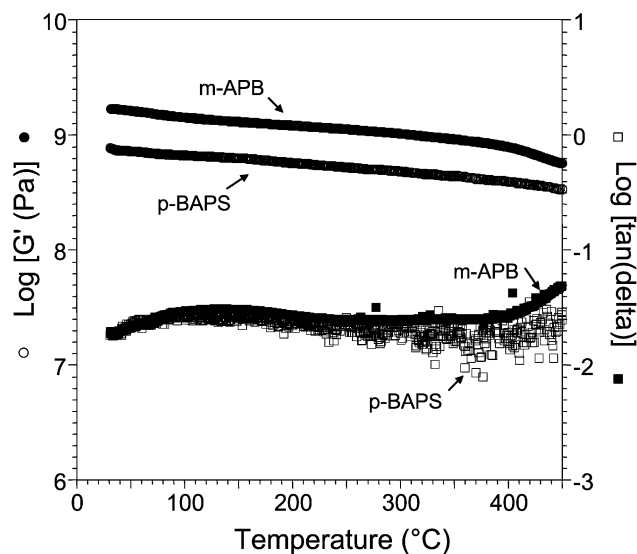
Fig. 4. Storage modulus changes and the loss factor curves from 40 to 450 °C for **4** cured with 2.4 mol% of *m*-APB and *p*-BAPS under a flow of nitrogen.

appears to retain its structural properties up to 400 °C as evidence from the modulus and tan δ plots.

4. Conclusion

Resorcinol-based phthalonitrile **1**, 1,3-bis(3,4-dicyanophenoxy)benzene, melts at a temperature about 50 °C below that of 4,4′-bis(3,4-dicyanophenoxy)biphenyl, which is being evaluated for numerous aerospace and marine applications. The monomer **1** exhibits a large processing window and can be easily fabricated to shaped components in the presence of aromatic amine curing additives. The viscosity of the melt can be easily controlled as a function of the quantity of curing additive and temperature. As the amount of curing additive was increased, an enhancement in

thermal stability was observed. Even though a large processing window exists for **1**, high temperatures are necessary for conversion to a thermoset using an aromatic amine curing additive.

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