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Development of a new poly(phenylquinoxaline) for adhesive and composite applications

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Dedicated to Professor Ronald K. Eby on the occasion of his 70th birthday

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Abstract

An improved synthetic route to a previously prepared self-polymerizable poly(phenylquinoxaline) (PPQ) monomer mixture, i.e., 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline, was developed. The monomer mixture was then polymerized in stages in *N*-methyl-2-pyrrolidinone/toluene and in *N*-cyclohexyl-2-pyrrolidinone at elevated temperatures in the presence of potassium carbonate. Polymer samples were obtained that had intrinsic viscosities as high as 1.64 dl/g in *m*-cresol at 30.0 ± 0.1°C and glass transition temperatures (T_gs) of 250–252°C. Thin films of the PPQ had a room temperature (RT) tensile strength of 114 MPa, a RT Young's modulus of 3.7 GPa, and a RT elongation at break of 93%. The neat resin had a flexural modulus of 3.12 GPa, a fracture energy (G_{1c}) of 2170 J/m^2 and a titanium–titanium lap shear strength of 31.4 MPa at room temperature. The polymer melt underwent shear thinning at 320°C. The melt viscosity decreased from $10^5$to 10^6 Pa s to less than 10^4 Pa s as the frequency was increased from 10^{-2} to 10^2 rad/s. Carbon-fiber(T650)®-reinforced composites of the PPQ were prepared and their mechanical properties determined. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: Polyphenylquinoxaline; Self-polymerizable monomer; Aromatic nucleophilic substitution

1. Introduction

Poly(phenylquinoxalines) (PPQs) are a well-established class of high-performance thermoplastics with high chemical and thermal stability [1,2]. However, they have not found wide-spread use primarily due to the high cost of the aromatic tetraamines and tetraketones used in their synthesis. In fact, the tetraketones are not commercially available. The polymerizations are also run in an undesirable solvent, i.e. *m*-cresol.

A recent approach to overcoming these problems has been to incorporate a quinoxaline moiety into a monomer, which is subsequently polymerized. For example, bisphenate nucleophiles containing quinoxaline rings have been utilized in aromatic nucleophilic substitution polymerizations [3–5]. The pyrazine ring in the quinoxaline structure has also been used to activate sites for nucleophilic substitution in another series of polymerizations [6,7]. A self-polymerizable PPQ monomer that contains both a phenate nucleophile and a fluorine atom activated by a pyrazine ring for nucleophilic displacement has been prepared in this laboratory [8–10]. The A–B monomer, which exists as two isomers, 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline (**1a**) and 2-(4-hydroxphenyl)-3-phenyl-6-fluoroquinoxaline (**1b**), has been polymerized in *N*-methyl-2-pyrrolidinone (NMP) to high molecular weight (Scheme 1). The polymer is soluble in NMP, in marked contrast to most PPQs, which are only soluble in phenolic and chlorinated solvents.

This research was divided into two parts. The objective of the first part was to improve the synthetic route to the A–B monomer mixture and the polymerization procedure. The monomer was also to be extensively characterized. In the second part, the thermal, mechanical, adhesive and rheological properties of the PPQ were to be determined. The polymer was also to be evaluated as a matrix resin in carbon-fiber-reinforced composites.

2. Experimental

2.1. Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra

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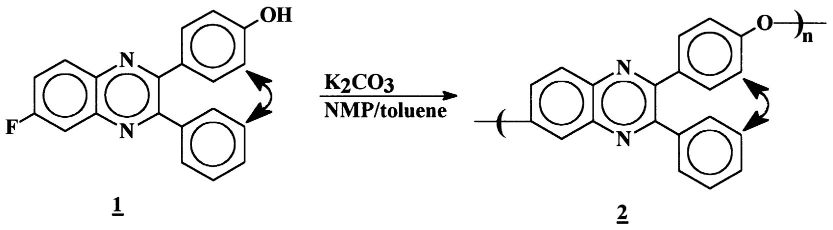


Scheme 1.

were obtained with a Varian Gemini 200 NMR Spectrometer at 200 MHz. Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were obtained with a Varian Gemini 300 NMR Spectrometer at 300 MHz. All melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were determined with a Cannon–Ubbelohde No.200 viscometer. Flow times were recorded for *m*-cresol solutions with polymer concentrations of approximately 0.5–0.25 g/dl at 30.0 ± 0.1°C. High-performance liquid chromatography (HPLC) analyses (Waters component system) were performed using a Micropak CH-18 column (30 mm × 4 mm) in 70/30 (vol/vol) acetonitrile/H_2O at a flow rate of 1.0 ml/min with a diode array detector (UV detector). Differential scanning calorimetry (DSC) analyses were performed in nitrogen with a heating rate of 10°C/min using a DuPont Model 9900 thermal analyzer equipped with a differential scanning calorimetry cell. Thermogravimetric analyses (TGA) were performed in both nitrogen (N_2) and air atmospheres with a heating rate of 10°C/min using a DuPont Model 951 thermogravimetric analyzer. Mechanical properties of neat resins, adhesives and composites were determined on a Model 1130 (or TT) Instron. The polymers were compression molded on a DAKE 100 klb heated press at 50–100°C above their T_g with the minimum pressure required for adequate flow. Melt viscosities were obtained on a Rheometrics Model RMS-800. A frequency sweep was used for dynamic measurements.

2.2. Monomer and intermediate syntheses

2.2.1. 4-(Phenylacetyl)anisole

A 2 l, three-necked, round-bottom flask equipped with an overhead stirrer and dropping funnel was charged with 900 ml of CS_2 and anisole (108.1 g, 1.000 mol). After the stirred solution was cooled to 0°C in an ice bath, $AlCl_3$ (160.0 g, 1.199 mol) was added. Phenylacetyl chloride (154.6 g, 1.000 mol) was then slowly added dropwise over 1 h. The mixture was stirred at 0°C for 1 h, allowed to warm to room temperature overnight, and then heated at reflux for an additional 1 h. The solution was allowed to cool to room temperature and then poured into 1 l of ice water and 40 ml of conc. HCl. Methylene chloride (CH_2Cl_2) (500 ml) was added to aid in the workup. The aqueous layer was separated and discarded. The organic layer was washed several times with water. After separating the organic layer, the solvent was removed under reduced pressure. The residue was taken up in 500 ml of cold ethanol. After 10–30 s, a white powder precipitated that was recrystallized from 95% ethanol to afford 132.0 g (60%) of white crystals: m.p. 68–70°C (lit. [11] 70.3–70.9°C), ^{1}H NMR δ 3.8 (s, 3H, OCH_3) 4.2 (s, 2H, CH_2) and 6.8–8.0 ppm (m, 9H, Ar).

2.2.2. 4-Methoxybenzil

A 2 l, three-necked, round bottom flask was charged with 4-(phenylacetyl)anisole (113.1 g, 0.5000 mol), 500 ml DMSO and 500 ml ethyl acetate, and $CuBr_2$ (223.4 g, 1.000 mol). The mixture was heated at reflux overnight. After cooling to room temperature, the solution was poured into 1 l of water. CH_2Cl_2 (500 ml) was then added. The aqueous layer was separated and discarded. The organic layer was washed with water until the aqueous layer was no longer green. The organic layer was separated, and the solvent was removed under reduced pressure. During this process, a silver-like solid precipitated. The solid was collected by filtration and discarded. The filtrate was reduced to dryness under reduced pressure, and the residue was recrystallized from methanol to yield 107.9 g (90%) of yellow crystals: m.p. 62–63°C (lit. [12] 62–63°C).

2.2.3. 4-Hydroxybenzil

4-Methoxybenzil (130.0 g, 0.5388 mol) was dissolved in a mixture of 1 l of 48% HBr and 500 ml of glacial acetic acid. The solution was heated at reflux for 4 h in a 2 l flask equipped with an overhead stirrer and a reflux condenser. After cooling to room temperature, the mixture was poured into 1 l of a slurry of ice and water. The precipitate that formed was collected by filtration, washed with water, dried in air, and then dissolved in 350 ml of a 10% NaOH solution. The solution was extracted three times with 120 ml portions of ether. The aqueous layer was acidified with conc. HCl. The precipitate that formed was collected by filtration, washed with water and recrystallized from benzene to yield 74.0 g (78%) of yellow crystals: m.p. 127–129°C (lit. [13] 127–129°C).

2.2.4. 1,2-Diamino-4-fluorobenzene

A solution of 4-fluoro-2-nitroaniline (65.90 g, 0.4221 mol) in 150 ml of ethyl acetate that contained palladium on activated carbon (5%, 0.81 g) was placed in a hydrogenation apparatus. The mixture was agitated under hydrogen (0.4 MPa) at room temperature for 4 h. The mixture was filtered, and the filtrate was evaporated to dryness on a rotary evaporator. The solid residue was recrystallized from toluene two times and sublimed under reduced pressure at 80°C to afford 48.0 g (90%) of a white powder: m.p. 89–91°C (lit. [14] 89–91°C).

2.2.5. 3-(4-Hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline (**1a**) and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline (**1b**)

To a 1 l, round-bottom flask equipped with an overhead stirrer and a reflux condenser were added 4-hydroxybenzil (73.12 g, 0.3232 mol), 1,2-diamino-4-fluorobenzene (40.77 g, 0.3232 mol), 500 ml of $CHCl_3$ and five drops of trifluoroacetic acid. The mixture was stirred and heated at reflux for 5 h. The solution was allowed to cool to room temperature, and washed with dilute HCl and then several times with water. After the solvent was removed under reduced pressure, the residue was recrystallized from 85% aqueous ethanol and then from toluene to yield 93.0 g (91%) of a mixture of bright yellow crystals and yellow powder: m.p. 126, 172°C (DSC); ^1H NMR ($CDCl_3$) δ 6.2 (1H, s, OH) and 8.1–6.7 ppm (12H, m, Ar).

2.3. Polymerizations

2.3.1. Self-polymerization of **1a** and **1b** in NMP

The isomeric mixture of 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline (25.0 g, 0.079 mol), K_2CO_3 (13.29 g, 0.095 mol), and 200 ml of a 1:1 (v/v) mixture of NMP/toluene were added to a 1 l, round-bottom flask equipped with an overhead stirrer, a N_2 inlet and a Dean–Stark trap. The reaction mixture was stirred and heated at 150°C for 4 h. During this period, water that formed was collected in the Dean–Stark trap. Toluene was removed by distillation as the reaction mixture was heated to 180°C for 1 h and then at 202°C for 2–3 h. The dark brown mixture was diluted with 200 ml of NMP, allowed to cool to room temperature and then added dropwise to 2 l of a 1:1 (v/v) methanol/acetic acid mixture. The fibrous, white PPQ that precipitated was collected by filtration, dried under reduced pressure, reprecipitated two times from $CHCl_3$ with methanol. After the polymer was successively stirred in refluxing methanol and water, it was dried at 180°C under reduced pressure for 20 h.

2.3.2. Self-polymerization of **1a** and **1b** in N-cyclohexyl-2-pyrrolidinone (CHP)

To a 500 ml, round-bottom flask equipped with an overhead stirrer, a condenser, a N_2 inlet and a Dean–Stark trap were added the isomeric mixture of 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline and 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline (25.0 g, 0.079 mol), K_2CO_3 (13.29 g, 0.095 mol) and 100 ml of CHP. The reaction mixture was stirred and heated at 150°C for 4 h. During this period, N_2 was purged rapidly through the reaction flask to remove the water that formed. The reaction mixture was heated at 180°C for 1 h and at 230°C for 2–3 h. The dark brown mixture was diluted with 100 ml of CHP, allowed to cool to room temperature and coagulated in 2 l of a 1:1 (v/v) methanol/acetic acid mixture. The fibrous, white PPQ that precipitated was collected by filtration, dried under reduced pressure, reprecipitated two times from $CHCl_3$ with methanol. After the polymer was successively stirred in refluxing methanol and water, it was dried at 180°C under reduced pressure for 20 h.

2.4. Determination of PPQ Properties

2.4.1. Fracture toughness (K_{1c}) measurments

A 4 in. × 2 in. mold that was filled with 7.0 g of polymer was placed in a hydraulic press and heated to the desired molding temperature with a heating rate of 3.5°C/min. At the processing temperature, which was usually 50–100°C above the PPQ T_g, 6.8 MPa of pressure was applied. Both the pressure and temperature were maintained for 20 min before the mold was allowed to cool to ambient temperature. The pressure was slowly removed once the temperature had fallen below the polymer T_g. Compression molded specimens were machined to size and notched down the middle. The samples were pre-cracked with a razor blade and tested using the double torsion method according to ASTM E399.

Load (P) was applied by a crosshead ram. The critical load at fracture (P_f) was obtained from a strip chart load–displacement curve. The tear path thickness (t_n) was measured with a traveling microscope.

Fracture toughness (K_{1c}) values were determined using plane strain conditions where $k = 3/(1 - \mu)$ and μ, Poisson's ratio, is assumed to be 0.35.

$$K_{1c} = P_f W_m [k/wt3t_n]^{1/2}$$

where w is the specimen width, t the specimen thickness, t_n the tear path thickness, W_m the length of torsion beam moment arm, and P_f the critical load at fracture.

2.4.2. Flexural modulus (E) measurements

One of the arms from a double torsion specimen was placed in a 3-point bend apparatus and tested. A load of about 10–15% of the maximum load to failure was applied to the specimen in a stepwise fashion. The load and the corresponding deflection were recorded. The procedure was repeated with replicate samples at least five times. The load (P) values were plotted versus deflection (R), and the initial slope ($m = P/R$) of the line was used in the following equation to calculate the flexural modulus:

$$E = s^3 m/4wt^3$$

where s is the support span, t the specimen thickness, w the specimen width, and P the load applied by the crosshead.

2.4.3. Fracture energy (G_{1c}) calculations

Fracture energy was calculated from the fracture toughness and flexural modulus (E):

$$G_{1c} = K_{1c}^2/E.$$

2.4.4. Determination of PPQ Ti–Ti lap shear strengths

A fiberglass scrim cloth was attached to a steel frame and heated to 100°C for 1 h under reduced pressure. The cloth was then lightly coated with a 10% (w/w) NMP solution of PPQ. After the coating was allowed to dry for 1 h at a temperature close to T_g under reduced pressure, a second coat was applied. Several additional applications of 10–20% (w/w) PPQ solutions were then made. The coated substrate was dried between applications. The procedure was repeated until the thickness of the coated cloth was 0.20–0.30 mm.

The titanium coupons were sand-blasted, washed with water and acetone, and dried in an oven at 60°C. The titanium was then treated twice with Pasagel 107. The second treatment was made approximately 10 min after the first. The coupons were then washed with deionized water and dried at 100°C for 1 h. The treated coupons were then coated three times with the 10–20% (w/w) PPQ solution. The coated coupons were dried at a temperature close to T_g under reduced pressure between applications. The impregnated cloth was placed between the two titanium strips. The specimens were placed in a compression molding device and heated at 355°C for 20 min under 6.8 MPa of pressure. The mold was then allowed to cool to ambient temperature. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

2.5. Preparation and testing of PPQ carbon-fiber-reinforced composites

2.5.1. Preparation of prepreg.

The carbon fibers were coated with a 20% (w/w) NMP solution of PPQ on a Model-30 Research Hot-Melt Prepregger. The fiber was wound around the rotating drum and covered with a backing sheet to produce a uniform prepreg. The prepreg was dried at 250°C for 2 h under reduced pressure. Rectangular sections (3 in. × 4 in.) were cut from the prepreg and dried under reduced pressure.

2.5.2. Flexural strength and modulus measurements

A stack of 21 uniaxially oriented samples of prepeg was placed in a mold and heated at 360°C for 1 h under 20.7 MPa of pressure. The specimens for the flexural strength and modulus measurements were 80 mm × 12.7 mm × 3 mm.

The specimens were tested using a 3-point bend method according to ASTM D790. Each specimen was supported at two points and loaded at midpoint. In this test, the maximum stress in the outer fibers occurs at midspan. This stress may be calculated for any point on the load-deflection curve using the following equation:

$$S = 3PL/2bd^2$$

where S is the stress in the outer fibers at midspan in N/m^2 (psi), P the load at a given point on the load–deflection curve in N, L the support span in m (in.), b the width of beam tested in m (in.), and d the depth of beam tested in m (in.).

The modulus of elasticity is the ratio, within the elastic limit, of stress to the corresponding strain and is usually expressed in N/m^2. It is calculated by first drawing a tangent to the steepest initial straight-line portion of the load–deflection curve and then using the following equation:

$$E = L^3m/4bd^3$$

where E is the modulus of elasticity in bending in N/m^2 (psi), L the support span in m (in.), b the width of beam tested in m (in.), d the depth of beam tested in m (in.), and m the slope of the tangent to the initial straight-line portion of the load–deflection curve in N/m (lbf/in.) of deflection.

2.5.3. Interlaminar shear strength (short beam) measurements

A stack of 44 dried uniaxially oriented samples of prepreg was placed in a mold and heated at 360°C for 1 h under a pressure of 20.7 MPa. The specimens for the interlaminar shear strength measurements were 32 mm × 6.4 mm × 6.4 mm. The specimens were tested using a 3-point bend method according to ASTM D2344. The apparent shear strength was calculated using the following equation:

$$S_H = 0.75P_B/bd$$

where S_H is the shear strength in N/m^2 (psi), P_B the breaking load in N (lbf), b the width of specimen in m (in.), and d the thickness of specimen in m (in.).

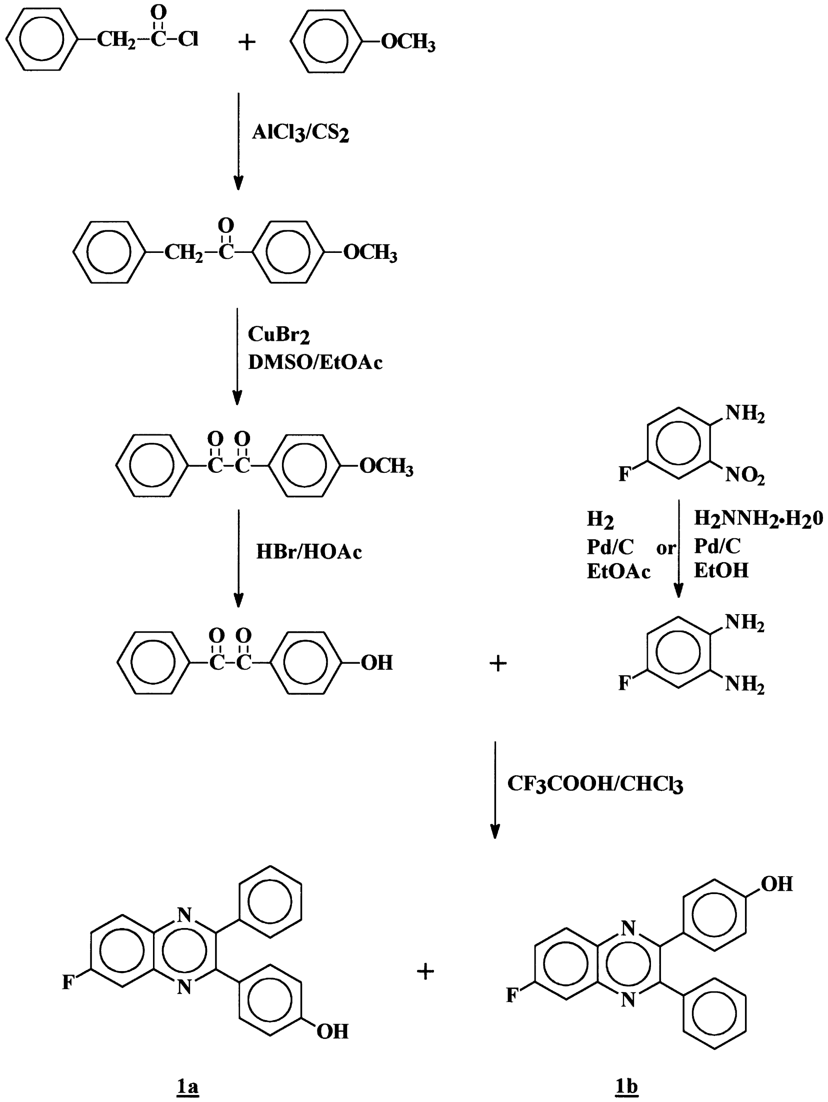
2.5.4. Tensile strength and modulus measurements

A stack of 18 dried uniaxially oriented samples of prepreg was placed in a mold and heated at 360°C for 1 h under a pressure of 20.7 MPa. The specimens were made and tested according to ASTM D3039. The specimens for the tensile property measurements were 12.7 mm × 127.0 mm × 2.54 mm. Grips for holding the test specimen between the fixed member and the movable member of the Instron were aligned along the longitudinal axis of the specimen. Each specimen was equipped with a minimum of three longitudinal strain gauges, two on the front face across the width and one on the back face of the specimen. These gauges gave a measure of bending in the thickness and width planes.

The tensile strength was calculated by the following equation:

$$S = P/bd$$

where S is the ultimate tensile strength in MPa (psi), P the



Scheme 2.

maximum load in N (lbf), *b* the width in mm (in.), and *d* the thickness in mm (in.).

The modulus of elasticity was calculated using the following equation:

$$E = (\Delta P/\Delta l)(l/bd)$$

where *E* is the modulus of elasticity in MPa (psi), $\Delta P/\Delta l$ the slope of the plot load as a function of deformation within the linear portion of the curve, *l* the gage length of the measuring instrument in mm (in.), *b* the width in mm (in.), and *d* the thickness in mm (in.).

2.5.5. Compressive strength and modulus measurements

A stack of 18 dried uniaxially oriented samples of prepreg was placed in a mold and heated at 360°C for 1 h under a pressure of 20.7 MPa. The specimens were made and tested according to ASTM D3410. The specimens for the compressive strength and modulus measurements were 137.7 mm × 6.35 mm × 3.0 mm.

The compressive strength was calculated using the following equation:

$$S = P/bd$$

where *S* is the ultimate compressive strength in MPa (psi), *P* the maximum load in MN (lbf), *b* the width in m (in.), and *d* the thickness in m (in.).

The initial modulus of elasticity, *E* (GPa, ksi), was calculated from the slope of the initial, straight line portion of the stress–strain curve:

$$E = \Delta\sigma/\Delta\varepsilon$$

where $\Delta\sigma$ is the change in compression stress in MPa (psi) and $\Delta\varepsilon$ the corresponding change in compression strain in m/m (in./in.).

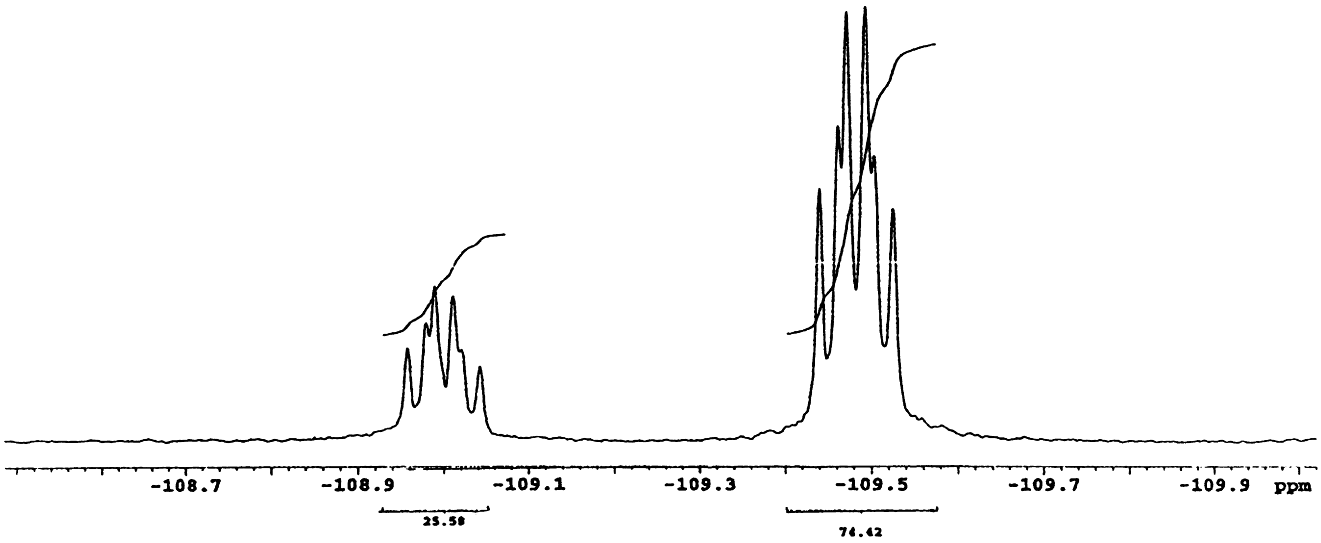
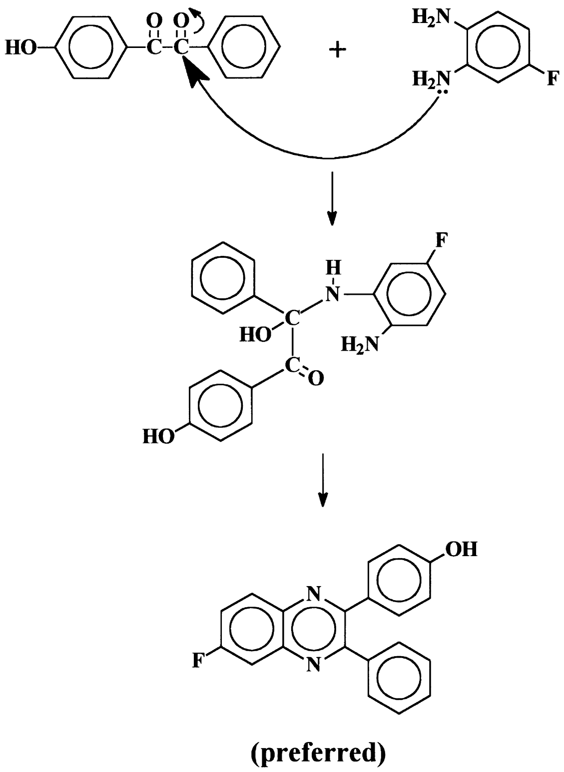


Fig. 1. ^{19}F NMR spectrum of the PPQ monomer mixture.

2.6. Determination of rheological properties

The rheological properties were determined using dynamic measurements that employed a frequency sweep at 320°C on a RMS-800 with a parallel plate fixture. The testing was carried out in the frequency range of 10^{-2}–10^{3} rad/s and at 2% strain.



Scheme 3.

3. Results and discussion

3.1. Monomer synthesis

The A–B PPQ monomer mixture (**1**) was first synthesized in 1989 by Harris and Korleski [8] in 11% overall yield using a four-step synthetic sequence. This route started with a mixed benzoin condensation of benzaldehyde and anisaldehyde to afford 4-methoxybenzoin, which was oxidized to 4-methoxybenzil. This intermediate was demethylated with hydrogen bromide to 4-hydroxybenzil, which was condensed with 1,2-diamino-4-fluorobenzene. The monomer mixture was also later prepared by Labadie and coworkers [15].

In an attempt to improve the overall yield of the Korleski route, 4-hydroxybenzil was prepared by a Friedel–Crafts acylation reaction (Scheme 2). Thus, 4-(phenylacetyl)anisole was obtained in greater than 60% yield from the reaction of phenylacetyl chloride and anisole in carbon disulfide in the presence of aluminum chloride. 4-(Phenylacetyl)anisole was oxidized to 4-methoxybenzil with copper(II)bromide in dimethylsulfoxide and ethyl acetate. The remainder of the reaction sequence was the same as previously reported [8–10]. The overall yield of this sequence was three times that of the previous route.

In order to obtain a pure monomer mixture, it was found that 1,2-diamino-4-fluorobenzene had to be sublimed under reduced pressure immediately prior to use. Polymers with low intrinsic viscosities were obtained when monomer mixtures were used that were prepared from diamine that had not been sublimed. It was also important that the chloroform solution in which the monomer was prepared was extracted with water prior to the monomer isolation. The monomer mixture was recrystallized from an ethyl acetate/hexanes mixture, 85% ethanol or toluene. Two recrystallizations were required in order to obtain a material that

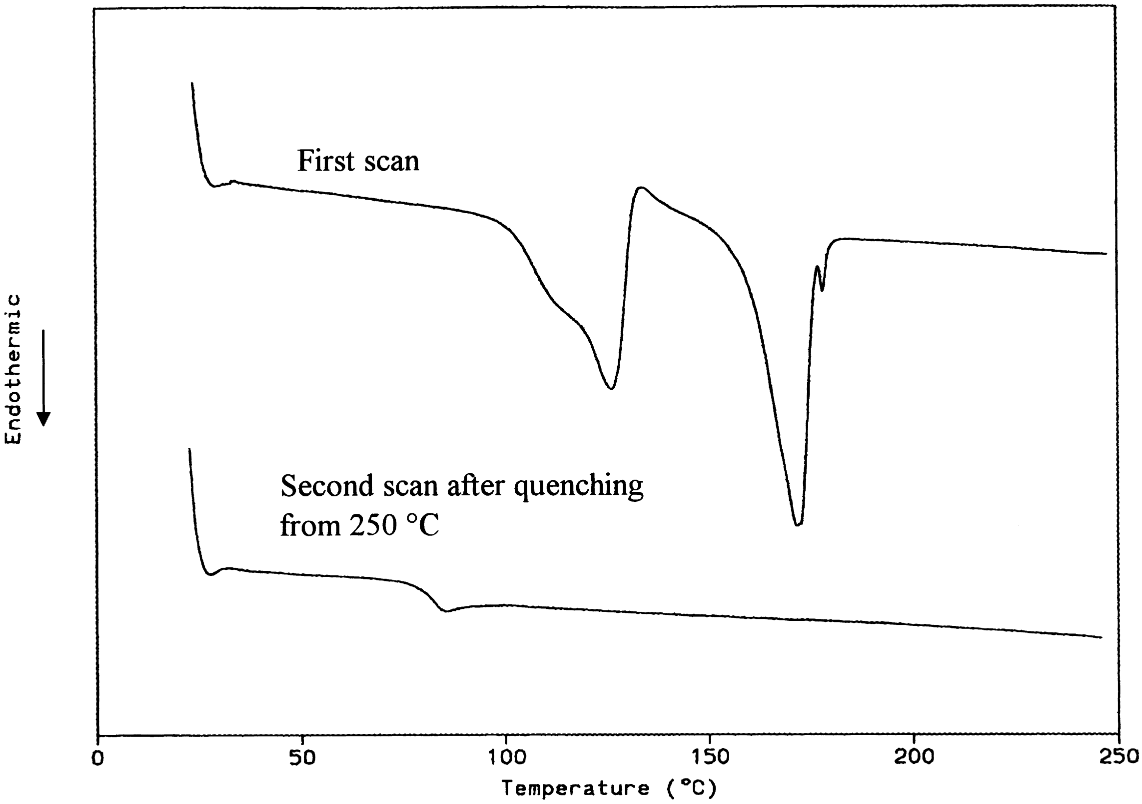


Fig. 2. DSC thermograms of the PPQ monomer mixture obtained with a heating rate of 10°C/min.

displayed only one distinct spot at $R_f = 0.64$ on TLC plates eluted with a 30/70 (v/v) ethyl acetate/hexanes mixture. HPLC analysis also confirmed the presence of only one component.

The structure of the monomer was confirmed by ^{1}H NMR and elemental analysis. The presence of two isomers was also confirmed by ^{19}F NMR (Fig. 1). Integration of the area under the two distinct multiplets centered at $-$ 109.0 and $-$ 109.5 ppm showed that the ratio of isomers was approximately 25:75. The multiplet centered at $-$ 109.5 ppm was attributed to the more symmetrical isomer **1b**. The fluorine atom in this isomer can be shielded by direct resonance with the hydroxyl group on the phenyl ring located at the 2-position. The formation of this isomer would also be expected to be favored by the differences in the reactivities of the carbonyl groups in 4-hydroxybenzil and the amino groups in 1,2-diamino-4-fluorobenzene. The electron-donating hydroxyl group in the benzil increases the electron density in the carbonyl group located closest to it. This makes the carbonyl less susceptible to nucleophilic attack than the adjacent carbonyl group. Likewise, the electron-withdrawing fluorine atom in the diamine decreases the electron density in the para-amino group, thus, making it less nucleophilic than the adjacent amino group (Scheme 3).

The DSC thermogram of the monomer mixture contained two strong melting endotherms with minima at 126 and 172°C and a weak endotherm with a minimum at 178°C (Fig. 2). When the sample was rapidly cooled from 250°C and again subjected to DSC analysis, a baseline shift indicative of a T_g appeared at 83°C. It was postulated that the initial multiple endotherms were due to different crystalline forms. It was also speculated that the mixture was trapped in an amorphous state when it was quenched from 250°C. To test these hypotheses, the amorphous sample was recrystallized from toluene and subjected to DSC analysis. The DSC thermogram was essentially identical to that obtained initially indicating that crystallization had occurred.

3.2. Self-polymerization of the A–B monomer mixture

The monomer mixture (**1**) was self-polymerized in a 1:1 (v/v) NMP/toluene mixture containing potassium carbonate (K_2CO_3) using a modification of a procedure previously used to prepare poly(aryl sulfones) [16]. Thus, the polymerization was carried out for 4 h at 150°C, during which time the water generated by the reaction of K_2CO_3 with the phenol was removed as a toluene azeotrope. The reaction mixture was then heated at 180°C for 1 h and finally at 202°C for 2–3 h. The final stage at 202°C was necessary to obtain high-molecular-weight polymer. The dark brown mixture was diluted with NMP to two times the original volume and coagulated in a 1:1 (v/v) acetic acid/methanol mixture. The fibrous white polymer that precipitated was reprecipitated from chloroform ($CHCl_3$) with methanol. The polymer was repeatedly stirred in methanol heated at reflux and in water heated at reflux to remove residual

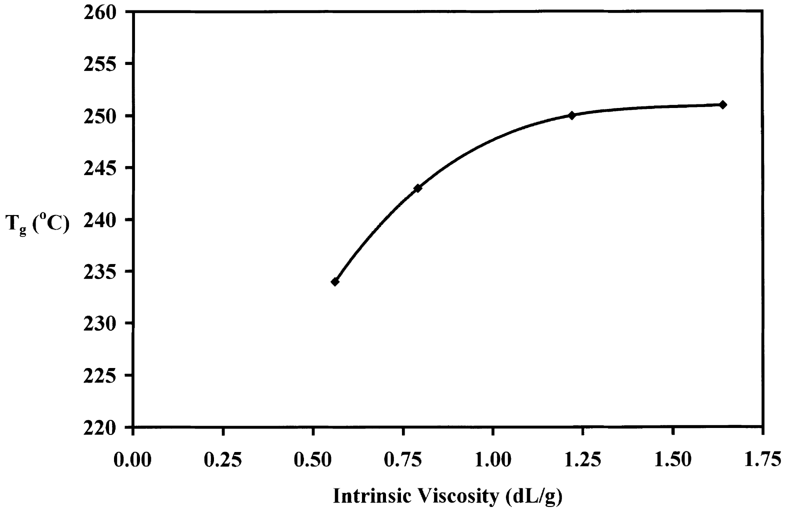


Fig. 3. Effect of intrinsic viscosity on the T_g of the PPQ.

solvent. The intrinsic viscosity of the PPQ (**2**), which was obtained in essentially a quantitative yield, ranged from 0.5 dl/g to as high as 1.64 dl/g (*m*-cresol at 30.0 ± 0.1°C) depending on the monomer purity. The intrinsic viscosity of polymer prepared from monomer purified by the procedure described in the previous section ranged from 1.3 to 1.64 dl/g.

It is important to note that heating at 202°C for longer periods of time resulted in a decrease in the PPQ intrinsic viscosity. In fact, when the polymerization was allowed to proceed at 202°C overnight, the solution turned dark green, and the product had an intrinsic viscosity of < 0.2 dl/g. It is postulated that depolymerization occurred via the attack of the excess carbonate groups along the polymer backbone. It is speculated that carbonate groups displaced phenate groups via aromatic nucleophilic substitution reactions. Polysulfones have been shown to be depolymerized by strong base (NaOH) via such reactions in 1 h at 165°C [17]. It is also possible that the fluoride ion was involved in the depolymerization process. Fluoride ion is a powerful nucleophile in dipolar aprotic solvents, although the solubility in these solvents is low [18]. A polyethersulfone has been shown to depolymerize to an equilibrium controlled molecular weight in sulpholane saturated with potassium fluoride at 200°C [19]. The fact that the PPQ degrades to such low molecular weight, however, suggests that a process is taking place where the chain fragments are terminated with groups that are not capable of undergoing reaction.

Table 1
Neat resin mechanical properties

Intrinsic viscosity of sample (dl/g)	Molding temperature (°C)	Flexural modulus *E* (GPa)	Fracture energy G_{1c} (J/m^2)
1.27	340	3.12	2170
0.66	290	1.24	1360

In order to determine if the polymerization could be carried out at higher temperatures, the monomer mixture was polymerized in *N*-cyclohexyl-2-pyrrolidone (CHP). The step-wise procedure used with NMP/toluene was followed, but in this case the solution was heated at 230°C during the final stage. Toluene was not used because, CHP is immiscible with water above 80°C, it is an effective dehydrating agent. The intrinsic viscosities of the PPQ samples obtained under these conditions ranged from 0.85 to 1.1 dl/g. Thus, the increase in polymerization temperature from 202 to 230°C resulted in slightly lower molecular weight polymer.

3.3. PPQ properties

3.3.1. Thermal properties

Thin films were prepared from 10–15% (w/w) solutions of the polymer in $CHCl_3$ and NMP. In order to determine the effect of molecular weight on T_g, films were prepared from samples with intrinsic viscosities that ranged from 0.55 to 1.64 dl/g. DSC thermograms were obtained on the films after they had been heated to 280°C and rapidly quenched to ambient temperature. As shown in Fig. 3, the T_g of this PPQ appears to be very molecular weight dependent below an intrinsic viscosity of about 1.0–1.1 dl/g (*m*-cresol at 30.0 ± 0.1°C). The T_g of high molecular weight PPQ is in the range of 250–252°C. Thus, the polymer has a T_g higher than that of most commercial thermoplastics such as polysulfone (190°C), polyethersulfone (230°C), and polyetherimide (217°C). The T_g is similar to that Mitsui Toatsu's Aurum® polyimide (250°C).

The thermal stability of a sample of PPQ **2** with an intrinsic viscosity of 1.27 dl/g was determined using thermogravimetric analysis (TGA) and isothermal gravimetric analysis (ITGA). The temperatures at which 5% weight losses occurred in N_2 and in air during TGA were 569 and 546°C, respectively. The ITGA thermograms of a sample

Table 2
Lap shear strengths (Ti–Ti) of PPQ **2**

Intrinsic viscosity of sample (dl/g)	Lap shear strength (MPa)	
	Room temperature[a]	232°C[a]
1.27	31.4	18.6
0.66	20.0	NA

[a] Test temperature.

with an intrinsic viscosity of 1.0 dl/g obtained in air at 355 and at 370°C showed less than 1.0% weight losses after 20 h. Thus, PPQ **2** has excellent stability and a wide gap between its T_g and its decomposition temperatures.

3.3.2. Thin film mechanical properties

Thin films (0.040–0.060 mm thick) were prepared from $CHCl_3$ solutions of a sample of **2** with an intrinsic viscosity of 1.64 dl/g. Dumb-bell shaped samples were cut from the films and tested according to ASTM D638. The films displayed a room temperature (RT) tensile strength of 114 MPa, a RT Young's modulus of 3.7 GPa, and a RT elongation of 93%. The value of the tensile strength is comparable to that of PPQs (117 MPa) prepared from tetraketones and tetraamines [1]. However, the modulus and elongation are considerably higher than those of conventional PPQs (2.62 GPa and 8.5%, respectively).

3.3.3. Neat resin mechanical properties

Samples of PPQ **2** were compression molded, machined to size, and their moduli and fracture energies (G_{1c}) determined using an Instron Model 1130 and a double torsion test (Table 1). The fracture energy of a sample with an intrinsic viscosity of 1.27 dl/g was 2170 J/m^2, while the fracture energy of a sample with an intrinsic viscosity of 0.66 dl/g was only 1360 J/m^2.

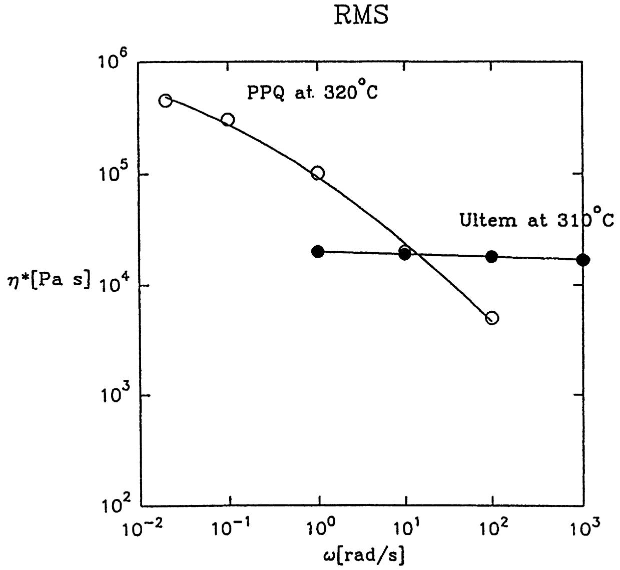


Fig. 4. Melt viscosities of the PPQ and Ultem® polyetherimide as a function of frequency.

3.3.4. Adhesive properties

The objective of this portion of the research was to determine the potential of polymer **2** as an adhesive in aerospace applications. Thus, titanium–titanium (Ti–Ti) lap shear adhesion tests were performed on two samples of the polymer with different intrinsic viscosities ($[\eta] = 1.27$ and 0.66 dl/g). The sample with an intrinsic viscosity of 1.27 dl/g displayed excellent Ti–Ti lap shear strengths at room temperature and at 232°C (Table 2). In fact, the shear strengths are comparable to those of other PPQs [20].

3.3.5. Rheological properties

The melt viscosity of a sample of the PPQ with an intrinsic viscosity of 1.0 dl/g was determined as a function of frequency on a Rheometrics RMS-800 at 320°C with 2% strain (Fig. 4). For comparison, similar measurements were carried out on a commercial polyetherimide (Ultem®). As shown in Fig. 4, the melt viscosity of Ultem® was lower than that of PPQ **2** in the low frequency region and remained relatively constant over the frequency range examined. PPQ **2**, however, underwent shear-thinning as the frequency increased. Thus, in the high frequency region, the viscosity of the PPQ was lower than that of Ultem®.

3.4. Properties of carbon-fiber-reinforced PPQ composites

The objective of this portion of the research was to evaluate the properties of carbon-fiber-reinforced composites of PPQ **2**. Thus, carbon-fiber (Amoco T-650®) prepreg was prepared using a 20% (w/w) NMP solution of a PPQ sample with an intrinsic viscosity of 1.0 dl/g on a drum winder. The prepreg was dried to low volatile content, uniaxially laid up, and compression molded into laminates. The C-scans of the laminates indicated that they were well consolidated. The laminates were cut to the appropriate sizes for flexural, shear, tensile, and compressive property measurements (Table 3). The list of mechanical properties represents, to the best of our knowledge, the most thorough characterization of linear PPQ carbon-fiber composites ever carried out. Previous attempts to prepare such composites were hampered by the need to process from high-boiling *m*-cresol solutions. Thus, only limited PPQ/carbon fiber composite data has been published [20]. The composite properties

Table 3
Properties of PPQ/T-650® composites

Flexural strength (MPa)	820
Flexural modulus (GPa)	136
Interlaminar shear strength (MPa)	49
Tensile strength (MPa)	131
Tensile modulus (GPa)	162
Compressive strength (MPa)	710
Compressive modulus (GPa)	134

are not as good as those of similar thermoplastic polyimide composites [21]. However, they are quite promising considering only a short time was spent optimizing the fabrication procedure.

4. Summary and conclusions

An improved synthetic route and purification procedure have been developed for a self-polymerizable PPQ monomer mixture. A polymerization procedure for the monomer has also been developed that consistently provides polymer with an intrinsic viscosity higher than 1.3 dl/g (*m*-cresol at 30.0 ± 0.1°C). A study of the effect of the PPQ intrinsic viscosity on the polymer T_g has shown that the T_g (250–252°C) is relatively independent of the viscosity (molecular weight) above approximately 1.0 dl/g. Mechanical property measurements also suggest that the critical intrinsic viscosity for achieving polymer properties is near 1.0 dl/g. The melt viscosity of the amorphous PPQ, which undergoes shear thinning, at 320°C is in the range of those of commercial, high-performance thermoplastics. This temperature is over 100°C below the polymer decomposition temperatures. Thus, the PPQ is readily melt processable.

The tensile strength of the PPQ is comparable to the tensile strength of previously prepared PPQs. However, the polymer modulus and elongation are significantly higher than those of previous PPQs. The combination of high T_g and excellent mechanical properties makes the thermoplastic PPQ a good candidate for high-performance applications. For example, preliminary evaluations of the PPQ as a high temperature adhesive and as a matrix resin in carbon-fiber-reinforced composites have given promising results.

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