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Synthesis and properties of phenylethynyl-terminated, star-branched, phenylquinoxaline oligomers☆

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Abstract

The primary objective of this work was to prepare readily melt and solution processable phenylquinoxaline (PQ) oligomers that could be thermally crosslinked to solvent-resistant resins. Thus, a mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline (HPFQ) was used to prepare star-branched PQ oligomers end-capped with 4-fluoro-4′-phenylethynylbenzophenone (FPEB). 1,1,1-Tris(4-hydroxyphenyl)ethane (THPE) was used as the branching unit. The oligomer number-average molecular weights ($\bar{M}_n$s) as determined by size exclusion chromatography (SEC) were close to the calculated values of 2922, 4698, 6474, and 13,578 g/mol, and their intrinsic viscosities ranged from 0.16 to 0.57 dl/g (*m*-cresol at 30°C). The oligomers, which were quite soluble in common organic solvents, had glass transition temperatures (T_gs) that ranged from 181 to 233°C (DSC, $\Delta T = 20$°C/min). They also underwent an exothermic cure with maxima from 377 to 443°C. The T_gs of the cured oligomers ranged from 259 to 284°C depending on the oligomer $\bar{M}_n$ and the curing conditions. The oligomers had low melt viscosities, e.g. an oligomer (SPQ-46) with an $\bar{M}_n$ of 4816 g/mol (SEC) had a melt viscosity of 150 Pa s at 348°C. A cured thin film of SPQ-46, which was insoluble in common organic solvents, had a room-temperature (RT) tensile strength of 100 MPa, a RT modulus of 2358 MPa, and a RT elongation of 5.9%. A cured sample of SPQ-46 displayed a RT titanium–titanium lap shear tensile strength of 35.2 MPa. SPQ-46/carbon fiber(IM-7) composites were prepared that displayed a RT flexural strength of 1902 MPa, a RT modulus of 1.38 GPa and a RT open hole compressive strength of 433 MPa. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Polyphenylquinoxalines; Star-branched; Phenylquinoxaline oligomers

1. Introduction

Polyphenylquinoxalines (PPQs) are a well-established class of high performance thermoplastics with considerable potential for use in aerospace, microelectronic, and membrane applications [1–5]. However, they have not been commercialized primarily due to the high cost of their tetraamine and tetraketone monomers. The polymerizations are also run in an undesirable solvent, namely, *m*-cresol. Thus, there has been considerable research carried out aimed at developing alternative, less-expensive routes to these materials. One of the approaches to overcoming these problems has been to incorporate a preformed quinoxaline ring into a monomer, which is then polymerized via an aromatic nucleophilic substitution reaction. For instance, bisphenate salts containing quinoxaline rings have been polymerized with aromatic dihalides [6–9]. The quinoxaline ring has also been used to activate sites for aromatic nucleophilic substitution in another series of polymerizations [10,11]. These reactions afford high-molecular-weight PPQs in polar aprotic solvents such as *N*-methylpyrrolidinone (NMP).

A related recent approach has involved the utilization of a self-polymerizable PPQ monomer. Thus, a PPQ monomer mixture, i.e. 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline (HPFQ), was prepared in this laboratory and self-condensed via an aromatic nucleophilic substitution reaction [12–15]. Although the PPQ obtained displays excellent properties, it has a relatively high melt viscosity and high temperatures are required for processing.

One of the most successful approaches to enhancing the melt processability of high temperature polymers has involved the use of oligomers end-capped with reactive functional groups. These groups contain carbon–carbon

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multiple bonds that are capable of undergoing thermal polymerization reactions [16–25]. For high temperature applications, phenylethynyl groups are often preferred due to their high curing temperatures, which provide broad processing windows [24,25]. The major advantages of this approach are that the reactive oligomers possess low melt viscosities (better processability), and they can be thermally cured in the melt without the evolution of volatile by-products. Upon curing, many of the materials show high chemical resistance, excellent thermal stability, high glass transition temperatures (T_gs), and excellent mechanical properties.

The objective of this research was to enhance the melt processability of PPQs using a reactive oligomer approach. Since star-branched polymers have better flow properties than their linear analogs with the same molecular weight [26], it was postulated that star-branched, phenylquinoxaline (PQ) oligomers would have very low melt viscosities. Thus, the approach involved the synthesis of star-branched PQ oligomers end-capped with phenylethynyl groups. Oligomers with various number-average molecular weights ($\bar{M}_n$s) were prepared using appropriate amounts of the HPFQ monomer mixture relative to that of a branching unit. 1,3,5-Trihydroxybenzene and 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) were chosen as branching units. The oligomers were end-capped with 4-fluoro-4′-phenylethynylbenzophenone (FPEB) [27]. The characterization work included a determination of the oligomer rheological properties, the optimum curing conditions, and the properties of the cured star-branched thermosets.

2. Experimental

2.1. Instrumentation

Proton nuclear magnetic resonance (^{1}H NMR) spectra were obtained at 200 MHz on a Varian Gemini-200 nuclear magnetic resonance spectrometer. Fluorine nuclear magnetic resonance (^{19}F NMR) spectra were obtained with a Varian Gemini XL-400 nuclear magnetic resonance spectrometer. All measurements were carried out in either deuterated chloroform ($CDCl_3$) or deuterated dimethyl sulfoxide [$(CD_3)_2SO$] with tetramethylsilane (TMS) as an internal standard. Infrared (IR) spectra were obtained with an ATI Mattson Genesis Fourier Transform Infrared Spectrophotometer. Solid samples were imbedded in KBr disks. The IR spectra of the polymers were obtained directly from their films. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN. All melting points were determined on a Mel-Temp melting point apparatus and are uncorrected. Intrinsic viscosities were measured with a No. 200 Cannon-Ubbelohde viscometer immersed in a water bath at 30.0 ± 0.1°C. Flow times were recorded for polymer solutions in *m*-cresol with polymer concentrations of approximately 0.5–0.25 g/dl. High performance liquid chromatography (HPLC) analyses (Waters component system) were performed using a Micro-Pak CH-18 column (30 mm × 4 mm) in an acetonitrile/H_2O solvent mixture with a flow rate of 1.0 ml/min using a diode array detector (UV detector). Size exclusion chromatography (SEC) analyses were performed using a series of ultrastyragel columns (50, 10^2, 10^3, 10^4 and 10^5 nm) in THF at 35°C or HT ultrastyragel columns (10^2, 10^3, 10^4 and 10^5 nm) in $CHCl_3$ at 40°C with a flow rate of 1 ml/min using UV, refractive index and light scattering detectors. SEC analysis on sample **16c**(SPQ-46) was performed in NMP at NASA Langley using a linear Waters styragel HT 6E column covering the molecular weight range of 10^3 to 10^7 g/mol in series with a styragel HT 3 column covering the molecular weight range of 10^2 to 10^4 g/mol. Molecular weights and molecular weight distributions of linear and star-branched oligomers were determined using a universal calibration curve, which was obtained by plotting $\ln([\eta]\bar{M}_n)$ as a function of elution volume, after calibration with standard polystyrene (Polymer Laboratories) samples. Differential scanning calorimetry (DSC) analyses were performed in a nitrogen atmosphere with a heating rate of 20°C/min using a Dupont Model 2910 thermal analyzer in combination with a differential scannning calorimetry cell. The T_g was taken as the midpoint in the inflection in the slope in the DSC trace. Approximately 12 mg of sample was placed in a sealed aluminum pan for each run. Thermogravimetric analyses (TGAs) were performed in both nitrogen (N_2) and air atmospheres with a heating rate of 10°C/min using a TA Instruments Hi-Res TGA 2950 thermogravimetric analyzer in combination with a 951 TGA cell. Approximately 15 mg of sample was used for each run. The polymers were compression molded on a DAKE 100 Klb heated press at 50–100°C above their T_gs with the minimum pressure required for adequate flow. Tensile properties of thin films were determined on a Model 1130 Instron with a crosshead separation speed of 1 mm/min. Melt viscosities were obtained on a Rheometrics Model RMS 800 using a frequency sweep from 10^{-2} to 10^2 rad/s.

2.2. Monomer and intermediate syntheses

2.2.1. 4-(Phenylacetyl)anisole [28,29] (*3*)

To a 2-l, three-neck, round-bottom flask equipped with an overhead stirrer and a nitrogen inlet–outlet were added 154.6 g (1.000 mol) of phenylacetyl chloride, 108.1 g (1.000 mol) of anisole, and 600 ml of *o*-dichlorobenzene. After the mixture was cooled to 0°C in an ice bath, 160 g (1.20 mol) of anhydrous $AlCl_3$ was added over a period of 2.5 h. After the addition, the mixture was further stirred at room temperature for 16 h. The solution was then poured into a slurry of 500 ml of water, 500 g of crushed ice, and 40 ml of concentrated HCl. The aqueous layer was separated and discarded. The organic layer was washed three times with water. The solvent was removed by distillation under reduced pressure. The orange residue was recrystallized from 95% ethanol to yield 189.0 g (84%) of white crystals: m.p. 74–76°C (Lit. [15] m.p. 68–70°C); ^{1}H NMR ($CDCl_3$) 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-Hydroxybenzil (**5**)

To a 1-l, three-neck, round-bottom flask equipped with an overhead stirrer and a reflux condenser were added 39.0 g (0.184 mol) of 4-(phenylacetyl)phenol, 200 ml of DMSO, 200 ml of ethyl acetate, and 84.0 g (0.376 mol) of $CuBr_2$. The mixture was stirred and heated at reflux for 14 h. After the reaction mixture was cooled to room temperature, it was poured into 500 ml of water. After 200 ml of CH_2Cl_2 was added, the organic layer was separated and washed with water until the aqueous layer was colorless. The organic layer was again separated, and the solvent was evaporated under reduced pressure on a rotary evaporator. The residue was dissolved in boiling toluene, filtered, and recrystallized from toluene to afford 37.0 g (88%) of yellow crystals m.p. 127–129°C (Lit. [30] m.p. 127–129°C).

2.2.3. 1,2-Diamino-4-fluorobenzene [31] (**7**)

To a hydrogenation bottle were added 66.0 g (0.423 mol) of 4-fluoro-2-nitroaniline, 150 ml of ethyl acetate, and 0.82 g of 5% palladium on activated carbon. The bottle was secured on a Parr hydrogenation apparatus and 60 psi of hydrogen was introduced. The mixture was then agitated at room temperature for 4 h. During the hydrogenation process, the hydrogen pressure was maintained at 60 psi. The resulting mixture was filtered under reduced pressure through a sintered glass funnel, and the filtrate was evaporated to dryness under reduced pressure on a rotary evaporator. The dark solid residue was sublimed under reduced pressure at 80°C to give 48.0 g (90%) of white crystals: m.p. 89–91°C (Lit. [31] m.p. 89–91°C).

2.2.4. 4-(Phenylacetyl)phenol (**10**)

To a 1-l, three-neck, round-bottom flask equipped with an overhead stirrer, a dropping funnel and a nitrogen inlet–outlet were added 46.4 g (0.300 mol) of phenylacetyl chloride, 80.0 g (0.600 mol) of anhydrous $AlCl_3$, and 200 ml of *o*-dichlorobenzene. The mixture was cooled to 0°C in an ice bath. A solution of 56.4 g (0.600 mol) of phenol in 200 ml of *o*-dichlorobenzene was added dropwise over 1 h. The temperature of the mixture was maintained below 5°C during the addition. The resulting mixture was stirred at room temperature for 1 h, heated at 125°C for 4 h, and allowed to cool to room temperature overnight. The solution was then poured into 500 ml of a 1:1 (v/v) mixture of HCl/H_2O. The organic layer was separated and washed with water. The solvent was removed under reduced pressure on a rotary evaporator to give a brown solid residue, which was recrystallized from a 5.5:4.5 (v/v) mixture of $CHCl_3$/ethyl acetate to yield 49.0 g (78%) of yellow crystals: m.p. 148–151°C (Lit. [32] m.p. 148°C); ^{1}H NMR ($CDCl_3$) δ 4.2(s, 2H, $-CH_2-$), 6.5 (s, 1H, –OH), 6.85 (d, 2H, Ar), 7.3 (m, 5H, Ar), and 7.95 ppm (d, 2H, Ar).

2.2.5. 2-(4-Hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-Hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline [12–14] (HPFQ) (**8a,b**)

To a 1-l, three-neck, round-bottom flask equipped with an overhead stirrer and a reflux condenser were added 73.47 g (0.3248 mol) of 4-hydroxybenzil, 41.80 g (0.3314 mol) of 1,2-diamino-4-fluorobenzene, 500 ml of $CHCl_3$, and 5 drops of trifluoroacetic acid. The mixture was stirred and heated at reflux for 5 h. After cooling to room temperature, the solution was poured into a separating funnel and washed with acidic (HCl) water. The organic layer was separated, and the solvent was evaporated to dryness under reduced pressure on a rotary evaporator. The residue was recrystallized twice from 90% ethanol and dried under reduced pressure at 50°C for 16 h to yield 93.5 g (91%) of a yellow crystalline powder: m.p. 100–139°C (DSC, $\Delta T = 20$°C/min, two broad endotherms); ^{1}H NMR ($CDCl_3$) δ 6.2 (s, 1H, –OH), 7.1–7.6 (m, 10H, Ar), 7.8 (m, 1H, Ar), and 8.15 ppm (m, 1H, Ar).

2.2.6. 4-Bromo-4′-fluorobenzophenone [27] (**14**)

To a 250-ml, three-neck, round-bottom flask equipped with a nitrogen inlet–outlet and a reflux condenser were added 39.8 g (0.181 mol) of 4-bromobenzoyl chloride and 117.0g (1.217 mol) of fluorobenzene. The mixture was cooled to 0°C in an ice bath, and 27.0 g (0.202 mol) of anhydrous $AlCl_3$ was then added. The mixture was stirred at room temperature for 15 min, heated at reflux for 4 h, and then stirred at room temperature for 16 h. The resulting solution was poured into 2 l of a 1:1 (v/v) mixture of HCl/water, extracted with CH_2Cl_2, and dried over $MgSO_4$. The solution was filtered, and the solvent was evaporated under reduced pressure on a rotary evaporator. The residue was recrystallized from ethanol to give 43.0 g (86%) of white crystals: m.p. 106–107°C (Lit. [27] m.p. 108°C).

2.2.7. 4-Fluoro-4′-phenylethynylbenzophenone [27] (**15**)

To a 500-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet–outlet and a reflux condenser were placed 30.0 g (0.107 mol) of 4-bromo-4′-fluorobenzophenone, 0.2 g of triphenylphosphine, 0.1 g of CuI, 0.1 g of bis(triphenylphosphine)palladium(II) chloride, and 450 ml of triethylamine. The mixture was heated at reflux for 4 h, cooled to room temperature, and stirred for an additional 16 h. The mixture was poured into 2 l of a 1:1 (v/v) mixture of HCl/water. The precipitate that formed was collected by filtration and recrystallized from acetone to give 23.0 g (75%) of white crystals: m.p. 152–153°C (Lit. [27] m.p. 150–151°C).

2.3. PPQ and PQ oligomer syntheses

2.3.1. Linear PPQ from the self-polymerization of monomer (**8a,b**) [15]

To a 100-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet–outlet, a Dean-Stark trap and a condenser were added 5.00 g (0.0158 mol) of the isomeric mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline, 2.66 g (0.0192 mol) of K_2CO_3, and 40 ml of a 1:1 (v/v) mixture of NMP/toluene. The mixture was stirred and heated at 150°C for 4 h during which time the water that was generated was azeotropically distilled and collected in the Dean-Stark trap. The mixture was then heated at 180°C for 1 h during which time the remaining toluene was removed by distillation. Finally, the mixture was heated at 202°C for 3 h. The dark red mixture was diluted with 40 ml of NMP and was allowed to cool to room temperature. The solution was then added dropwise to 400 ml of a 1:1 (v/v) methanol/acetic acid mixture. The white fibrous polymer was collected by filtration, dried under reduced pressure, and reprecipitated twice from $CHCl_3$ with methanol. The polymer was successively stirred in boiling methanol and then in boiling water, filtered, and dried at 180°C under reduced pressure for 24 h.

2.3.2. Star-branched PQ oligomers with 1,3,5-trihydroxybenzene (THB) as the branching unit

2.3.2.1. Procedure A To a 50-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet–outlet, a Dean-Stark trap and a condenser were added 3.1634 g (10.000 mmol) of the isomeric mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline, 0.0449 g (0.277 mmol) of 1,3,5-trihydroxybenzene, 0.2495g (0.8300 mmol) of 4-fluoro-4′-phenylethynylbenzophenone, 1.63 g (11.8 mmol) of K_2CO_3, and 12 ml of a 1:1 (v/v) mixture of NMP/toluene. The mixture was stirred and heated at 150°C for 4 h during which time the water that was generated was azeotropically distilled and collected in the Dean-Stark trap. The mixture was then heated at 180°C for 1 h during which time the remaining toluene was removed by distillation. Finally, the mixture was heated at 202°C for 3 h. The dark red mixture was diluted with 32 ml of NMP and allowed to cool to room temperature. The solution was then added dropwise to 120 ml of a 1:1 (v/v) mixture of methanol/acetic acid. The white powdery polymer was collected by filtration, dried under reduced pressure, and reprecipitated twice from $CHCl_3$ with methanol. The polymer was successively stirred in boiling methanol and in boiling water, filtered, and dried at 180°C under reduced pressure for 24 h. SEC analyses indicated that the $\bar{M}_n$s of the samples were 4200 and 4380, with polydispersities (PDIs) of 2.35 and 3.66. The calculated $\bar{M}_n$ for the ratio of reactants used was 11,000 g/mol.

2.3.2.2. Procedure B To a 50-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet–outlet, a Dean-Stark trap and a condenser were added 5.0614 g (16.000 mmol) of the isomeric mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline, 0.0961 g (0.762 mmol) of 1,3,5-trihydroxybenzene, 2.658 g (19.23 mmol) of K_2CO_3 and 40 ml of a 1:1 (v/v) mixture of NMP/toluene. The mixture was stirred and heated at 150°C for 4 h during which time the water that was generated was azeotropically distilled and collected in the Dean-Stark trap. The mixture was then heated at 180°C for 1 h during which time the remaining toluene was removed by distillation. Finally, the mixture was heated at 202°C for 2 h. After 0.830 g (2.76 mmol) of 4-fluoro-4′-phenylethynylbenzophenone was added, the stirring was continued for an additional 1 h. The solution was diluted with 40 ml of NMP and was allowed to cool to room temperature. The dark red solution was then added dropwise to 400 ml of a 1:1 (v/v) mixture of methanol/acetic acid. The white fibrous polymer was collected by filtration, dried under reduced pressure, and reprecipitated twice from $CHCl_3$ with methanol. The polymer was successively stirred in boiling methanol and in boiling water, filtered, and dried at 120°C under reduced pressure for 24 h. Other ratios of the reactants were also used so that oligomers with calculated $\bar{M}_n$s of 2,700, 4,500, and 7,200 g/mol should have been obtained. However, SEC analysis indicated the product $\bar{M}_n$s ranged from 17,900 to 45,200 g/mol. The products also contained a low $\bar{M}_n$ fraction.

2.3.2.3. Procedure C: To a 50-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet-outlet, a Dean-Stark trap and a condenser were added 0.1994 g (1.581 mmol) of 1,3,5-trihydroxybenzene, 1.8342 g (13.271 mmol) of K_2CO_3, and 30 ml of a 1:1 (v/v) mixture of NMP/toluene. After the mixture was stirred and heated at 150°C for 1 h, 3.000 g (9.482 mmol) of the isomeric mixture of 2-(4-hydroxy-phenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxy-phenyl)-2-phenyl-6-fluoroquinoxaline was added. The solution was stirred at 150°C for 4 h during which time the water that was generated was azeotropically distilled and collected in the Dean-Stark trap. The mixture was then heated at 180°C for 1 h during which time the remaining toluene was removed by distillation. Finally, the mixture was heated at 202°C for 2 h. After 1.59 g (5.29 mmol) of 4-fluoro-4′-phenylethynylbenzophenone was added, the stirring was continued for an additional 1 h. The solution was diluted with 30 ml of NMP and was allowed to cool to room temperature. The dark red solution was then added dropwise to 600 ml of a 2:1 (v/v) mixture of acetone/acetic acid. The white powdery polymer was collected by filtration, dried under reduced pressure, and reprecipitated twice from $CHCl_3$ with methanol. The polymer was successively stirred in boiling methanol and in boiling water, filtered, and dried at 120°C under reduced pressure for 24 h. Another ratio of reactants was also used so that oligomers with calculated $\bar{M}_n$s of 2,700 and 4,500 g/mol should have been obtained. However, SEC analysis indicated that the product $\bar{M}_n$s were 8,300 and 23,300 g/mol. The products also contained a very low molecular weight fraction.

2.3.2.4. Procedure D To a 50-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet–outlet, a Dean-Stark trap and a condenser were added 0.0996 g (0.790 mmol) of 1,3,5-trihydroxybenzene, 1.705 g (12.34 mmol) of K_2CO_3, and 30 ml of a 1:1 (v/v) mixture of NMP/toluene. After the mixture was stirred and heated at 150°C for 2 h, 2.99 g (9.45 mmol) of the isomeric mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline was added. The solution was stirred at 150°C for 4 h during which time the water that was generated was azeotropically distilled and collected in the Dean-Stark trap. The mixture was then heated at 180°C for 1 h during which time the remaining toluene was removed by distillation. Finally, the mixture was heated at 202°C for 2 h. After 0.980 g (3.26 mmol) of 4-fluoro-4′-phenylethynylbenzophenone was added, the stirring was continued for an additional 1 h. The dark red solution was diluted with 30 ml of NMP and was allowed to cool to room temperature. The solution was then added dropwise to 600 ml of a 2:1 (v/v) mixture of acetone/acetic acid. The white powdery polymer was collected by filtration, dried under reduced pressure, and reprecipitated from $CHCl_3$ with methanol. The polymer was successively stirred in boiling methanol and in boiling water, filtered, and dried at 120°C under reduced pressure for 24 h. Although the calculated $\bar{M}_n$ for this ratio of reactants was 4,500 g/mol, SEC analysis indicated that the $\bar{M}_n$ was 26,500 g/mol. The product also contained a very low molecular weight fraction.

2.3.3. Star-branched PQ oligomers with 1,1,1-tris(4-hydroxyphenyl)ethane (THPE) as the branching unit (**16**)

To a 100-ml, three-neck, round-bottom flask equipped with an overhead stirrer, a nitrogen inlet–outlet, a Dean-Stark trap and a condenser were added 0.0577 g (0.188 mmol) of 1,1,1-tris(4-hydroxyphenyl)ethane (THPE), 1.310 g (9.478 mmol) of K_2CO_3, and 25 ml of a 1:1 (v/v) mixture of NMP/toluene. After the mixture was stirred and heated at 150°C for 1 h, 2.5000 g (7.9030 mmol) of the isomeric mixture of 2-(4-hydroxyphenyl)-3-phenyl-6-fluoroquinoxaline and 3-(4-hydroxyphenyl)-2-phenyl-6-fluoroquinoxaline was added. The solution was stirred at 150°C for 4 h during which time the water that was generated was azeotropically distilled and collected in the Dean-Stark trap. The mixture was then heated at 180°C for 1 h during which time the remaining toluene was removed by distillation. Finally, the mixture was heated at 202°C for 2 h. After 0.220 g (0.733 mmol) of 4-fluoro-4′-phenylethynylbenzophenone was added, the stirring was continued for an additional 1 h. The solution was diluted with 13 ml of NMP and allowed to cool to room temperature. The dark red solution was then added dropwise to 500 ml of a 10:1 (v/v) mixture of acetone/acetic acid. The white powdery polymer was collected by filtration, dried under reduced pressure, and reprecipitated from $CHCl_3$ with methanol. The polymer was successively stirred in boiling methanol and in boiling water, filtered, and dried at 100°C under reduced pressure for 48 h.

2.4. Adhesive specimens

Supported adhesive film (about 0.030 cm thick) with a volatile content of $<1\%$ was prepared by multiple brush coating a SPQ-46 NMP solution (35% w/w solids) onto 112 E-glass having an A-1100 finish and by drying after each coat to 200°C for 1 h in air. Standard lap shear adhesive specimens (bond area 2.54 cm wide × 1.27 cm overlap) using titanium (Ti, 6Al-4V) adherend with a Pasa-Jell 107 surface treatment were fabricated in a press with the final consolidation conditions of 350°C under contact pressure of 0.34 MPa for 1 h. Tensile shear strengths were determined according to ASTM D1002 using four specimens per test condition.

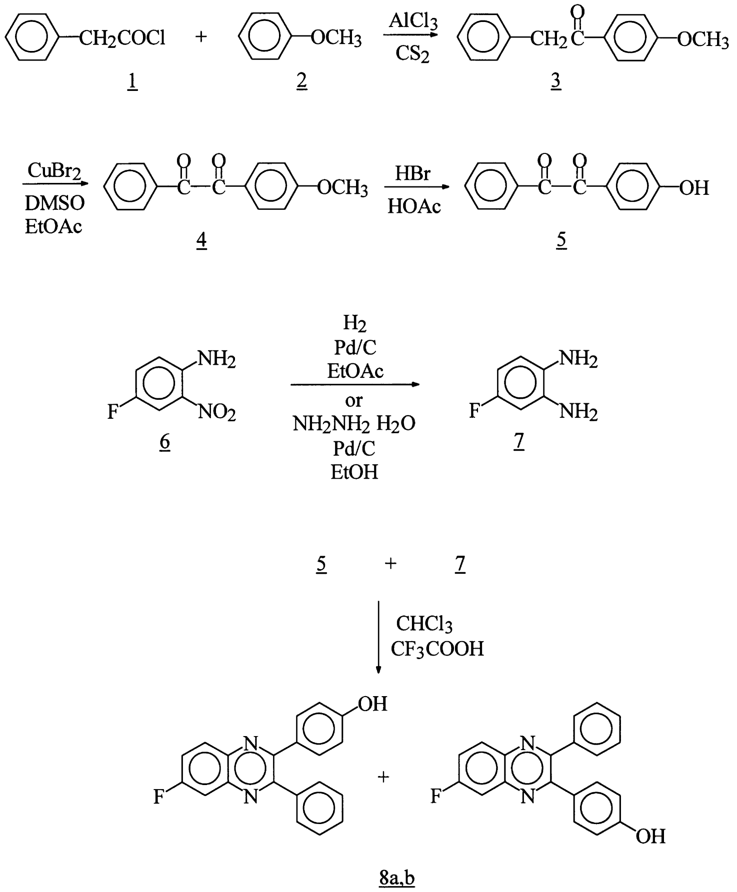
2.5. Composite specimens

An NMP solution (35% w/w solids) of the SPQ-46 oligomer was used to coat unsized IM-7 carbon fiber (12K tow) on a prepregging machine. The unidirectional tape (7.62 cm wide) exhibited a resin content of 33%, volatile content of about 19% (primarily NMP to provide handleability) and fiber aerial weight of about 145 g/m^2. Laminates were fabricated in a vacuum press under reduced pressure by heating to 250°C over about 1 h and holding at 250°C for 0.5 h. Contact pressure was subsequently applied and the temperature was ramped up over 0.5 h to 350°C and held for 1 h. The laminates were cooled under contact pressure to about 100°C, and the pressure was released. The laminates had resin contents of about 28% and void contents of about 3.8%. For flexural properties, the laminates had a unidirectional layup, whereas, the laminates for open hole compressive properties had a 42/50/8 layup (42% fiber orientation in the zero direction). The laminates were ultrasonically scanned (C-scanned), cut into specimens, and tested for flexural and open hole compressive properties according to ASTM D790 and a Northrop Grumman specification [33], respectively.

3. Results and discussion

3.1. PPQ Monomer (HPFQ) synthesis

The A-B PPQ monomer mixture HPFQ (**8a,b**) was first

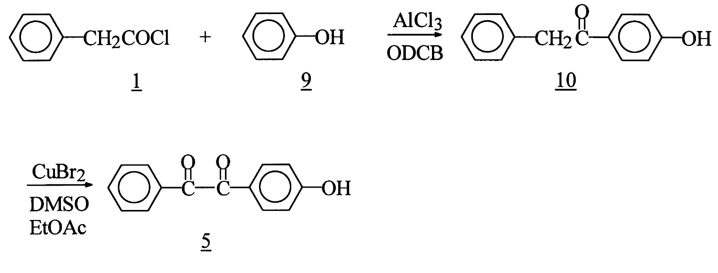


Scheme 1.

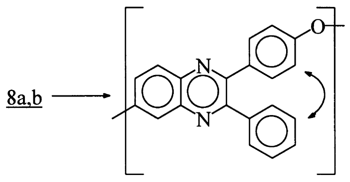
prepared in 1989 by Harris and Korleski [12–14] in 11% overall yield using a four step synthetic sequence. A more effective route to the self-polymerizable PPQ monomer was developed in 1993 by Harris and Kim [15] (Scheme 1). The overall yield of this route was three times that of the initial route. In this route, however, carbon disulfide (CS_2) was used in an initial Friedel–Crafts acylation reaction of phenylacetyl chloride with anisole. This solvent is undesirable due to its odor and low flash point. Thus, the immediate research objective was to find a more efficient and safer synthetic route to the HPFQ monomer.

The first approach was to modify Kim's acylation procedure by replacing CS_2 with *o*-dichlorobenzene (ODCB). The Friedel–Crafts acylation of anisole with phenylacetyl chloride in this solvent afforded an 84% yield of 4-phenylacetylanisole, which was higher than previously reported. In the new procedure, the anhydrous $AlCl_3$ was added slowly in 16 portions over 2 h at 0°C to a mixture of phenylacetyl chloride and anisole in ODCB. Since the solvent has a high boiling point of 180°C, it was removed by vacuum distillation. ODCB has been reported to be an excellent solvent for Friedel–Crafts acylations [34]. Unlike CS_2, ODCB was not flammable; therefore, the reaction was less hazardous. However, it was still necessary to cleave the intermediate to the corresponding phenol (**5**). To improve the process, a new route to **5** was then developed (Scheme 2).

The reaction of phenylacetyl chloride with excess phenol in ODCB in the presence of anhydrous $AlCl_3$ gave



Scheme 2.



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Scheme 3.

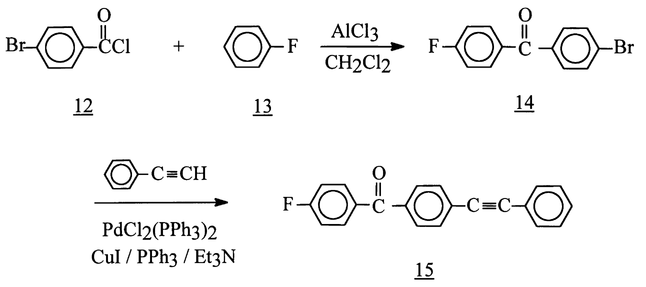
4-(phenylacetyl)phenol (**10**). The yield was dependent on the addition order. For example, only a 20% yield was obtained when phenylacetyl chloride was added to the mixture containing phenol and $AlCl_3$. In contrast, the addition of phenol to the mixture of phenylacetyl chloride and $AlCl_3$ gave a 78% yield. Oxidation of **10** with $CuBr_2$ and DMSO in ethyl acetate afforded **5** in 90% yield. The remainder of the reaction sequence was the same as Kim's route. The overall yield of HPFQ monomer (**8a,b**) was 62% as compared to the 38% reported by Kim [15].

The monomer mixture was recrystallized from 95% ethanol. To determine the purity, the monomer was subjected to HPLC analysis using a 30:70 (v/v) mixture of HPLC grade water/acetonitrile as the eluent, which showed that it was over 99.5% pure. The chemical structure of the monomer was further confirmed by ^{1}H NMR.

The purification of the intermediate 1,2-diamino-4-fluorobenzene (**7**) was also simplified. The crude product obtained from the hydrogenation of 4-fluoro-2-nitroaniline (**6**) was sublimed without recrystallization. In the previous procedure, the intermediate was recrystallized twice from toluene before sublimation. HPLC analysis showed that the product purified in this manner was over 99% pure, similar to that obtained previously.

3.2. Self-polymerization of HPFQ (**8a,b**)

In order to obtain an internal, linear PPQ standard, the self-polymerization of the monomer was carried out according to the Kim procedure (Scheme 3) [15]. The polymerization was conducted in a 1:1 (v/v) mixture of NMP/toluene in the presence of weak base K_2CO_3. The resulting PPQ (**11**) had an intrinsic viscosity of 1.46 dl/g and a T_g of 255°C (DSC, $\Delta T = 20$°C/min). TGA analysis of the polymer showed 5% weight losses at 534°C in nitrogen and at 533°C in air. The polymer was soluble in $CHCl_3$, *m*-cresol, and NMP. These properties are comparable to those of the PPQ obtained by Kim. Thin films of the polymer were cast from 10% (w/v) chloroform solutions, and their tensile properties were determined according to ASTM D-882. The films had RT ultimate tensile strength of 114 MPa, RT Young's modulus of 3.7 GPa, and RT elongation at break of 86%.



Scheme 4.

3.3. Synthesis of 4-fluoro-4′-phenylethynylbenzophenone (15)

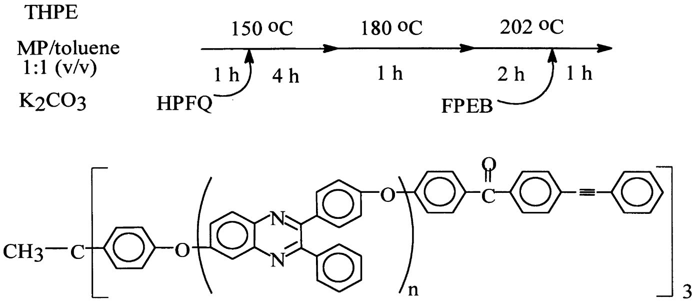
The objective of this portion of the research was to prepare an end-capping agent that could be used to terminate the chain ends of star-branched PQ oligomers. 4-Fluoro-4′-phenylethynylbenzophenone (FPEB, **15**) was synthesized using the known procedure (Scheme 4) [27]. Thus, Friedel–Crafts acylation of fluorobenzene (**13**) with 4-bromobenzoyl chloride (**12**) in the presence of $AlCl_3$ afforded 4-bromo-4′-fluorobenzophenone (**14**) in 86% yield. The intermediate **14** was treated with phenylacetylene in triethylamine in the presence of dichlorobis(triphenylphosphine)palladium(II), cuprous iodide, and triphenylphosphine to give the end-capping agent **15**. The product was obtained in 75% yield after recrystallization from acetone. Compound **15** was chosen for end-capping the PPQs, because it had been reported to be very reactive in aromatic nucleophilic displacement reactions [27]. The fluorine atom is activated for displacement by the electron-withdrawing carbonyl group in the *para*-position. The phenylethynyl group had been shown to be an excellent chain extender that undergoes a thermal addition reaction without the evolution of volatile by-products at a temperature high enough to provide a wide processing window [24,25,27].

3.4. PQ oligomers based on 1,3,5-trihydroxybenzene

The first branching unit to be evaluated in the synthesis of star-branched PPQs was the commercially available 1,3,5-trihydroxybenzene (THB). Various procedures were tried in order to determine the optimal conditions for the synthesis of well-defined, star-branched oligomers. However, numerous attempts to prepare the desired products using different modes of addition and different heating cycles were unsuccessful. In some cases, predominately linear oligomers were obtained with molecular weights lower than expected, while in others the product molecular weight was higher than expected. The results were also not reproducible.

3.5. PQ oligomers based on 1,1,1-tris(4-hydroxyphenyl)ethane

Since star-branched PQ oligomers free of linear PQ polymer were not obtained with THB, the use of a second branching unit, i.e. 1,1,1-tris(4-hydroxyphenyl)ethane (THPE), which is also commercially available, was



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Scheme 5.

investigated. Unlike THB in which all the hydroxy groups lie in the same plane of a benzene ring, THPE contains three 4-hydroxyphenyl moieties attached to an α-carbon of ethane in a distorted tetrahedral arrangement. Thus, the hydroxy groups in THPE are less sterically hindered than those in THB. The p*K*a values of THPE are also lower than the p*K*a values of THB. Therefore, the more acidic THPE is more prone to complete neutralization with a weak base. Both of these factors contribute to a phenate salt that is more active in nucleophilic substitution reactions.

In the procedure used to prepare the oligomers, a mixture containing the branching unit THPE, K_2CO_3, NMP, and toluene was heated at 150°C for 1 h in order to first convert the three hydroxy groups to the corresponding phenate salts (Scheme 5). The water was removed by distillation as a water/toluene azeotrope over 1 h. The monomer was then added, and the mixture was stirred at 150°C for 4 h. The remaining toluene was removed by distillation at 180°C. In the final step, the mixture was heated at 202°C for 2 h, the FPEB powder was added, and the heating was continued for 1 h. The solution was diluted with an equal volume of NMP and allowed to cool at room temperature. The product was isolated by precipitation in a 1:1 (v/v) mixture of methanol and acetic acid. Molar ratios of THPE:HPFQ:FPEB were employed that would afford PQ oligomers with calculated $\bar{M}_n$s of 2922, 4698, 6474, and 13,578 g/mol (Table 1). Because the end-capping agent did not dictate the molecular weight of the oligomer produced, it was added in excess in order to ensure that all the chain ends of the initially formed star-branched oligomers were end-capped. The excess end-capping agent, which is soluble in methanol, was removed during the precipitation process.

Table 1
Molar ratios of HPFQ, FPEB, and THPE used in the preparation of star-branched PQ oligomers **16a**–**d**

Star-branched oligomers	Calcd. $\bar{M}_n$ (g/mol)	Molar ratio		
		HPFQ	THPE	FPB
16a	2922	6	1	Excess
16b	4698	12	1	Excess
16c	6474	18	1	Excess
16c(SPQ-46)[a]	6474	18	1	Excess
16d	13,578	42	1	Excess

[a] A 100 g sample was also prepared for evaluation at theNASA Langley Research Center.

*3.6. Properties of star-branched PQ oligomers (**16a–d**)*

The star-branched oligomers **16a**–**d** had intrinsic viscosities that ranged from 0.16 to 0.57 dl/g (Table 2). Oligomers **16a**–**d** were soluble in $CHCl_3$, *m*-cresol, and NMP. Oligomers **16a**–**c** were also soluble in THF, whereas **16d** was not (Table 2). Thin films of the oligomers were cast from 10% (w/v) $CHCl_3$ solutions. The films of **16a**–**c** were very brittle and cracked during the process of solvent evaporation. However, a flexible film of **16d** was obtained by slow solvent evaporation. SEC analyses of the star-branched PQ oligomers **16a**–**c** were performed in THF at 35°C, whereas that of **16d** was performed in $CHCl_3$ at 40°C. SEC analysis of **16c**(SPQ-46) was carried out at NASA Langley in NMP. A relatively narrow Gaussian molecular weight distribution was observed for all the oligomers, having polydispersities (PDIs) that ranged from 1.2 to 1.8. In general, the PDIs increased as the oligomer $\bar{M}_n$s increased. The PDI of the large sample of **16c**(SPQ-46) was slightly higher than that of the small sample. This indicates that the reaction conditions, including the reactor design, can influence the PDI. The $\bar{M}_n$s determined by SEC analyses were in good agreement with the calculated values (Table 3).

The IR spectrum of **16d** was obtained on a thin film cast from a $CHCl_3$ solution. The strong carbonyl stretching absorption band near 1750 cm^{-1} provided evidence for the incorporation of the end-capping agent at the oligomer chain ends. The strong absorption peak at 1230 cm^{-1} was attributed to the stretching vibration band of the ether(-*o*-) linkages in the oligomer. The weak absorption band at around 2215 cm^{-1} was attributed to the stretching vibration of the ethynyl carbon-carbon triple bond in the Ar–C≡C–Ar moieties. The stretching vibration band at 2989 cm^{-1}, due to a C–H bond, was assigned to the sole methyl group of the branching unit in the oligomer.

The ^{1}H NMR spectrum of **16d**, which was obtained in

Table 2
Intrinsic viscosity, film properties, and solubility of star-branched PQ oligomers **16a–d**

Star-branched oligomers	$[\eta]$[a] (dl/g)	Film[b] properties	Solubility[c]			
			THF	$CHCl_3$	NMP	*m*-Cresol
16a	0.16	Brittle	+	+	+	+
16b	0.23	Brittle	+	+	+	+
16c	0.39	Brittle	+	+	+	+
16c(SPQ-46)	0.23[d]	Brittle	+	+	+	+
16d	0.57	Flexible	−	+	+	+

[a] Intrinsic viscosity in *m*-cresol at 30.0 ± 0.1°C.
[b] Cast from 10% chloroform solutions.
[c] + :A 10% (w/v) solution could be prepared; − : Only 2% (w/v) solutions could be prepared.
[d] Intrinsic viscosity in NMP at 30.0 ± 0.1°C.

$CDCl_3$, contained a broad singlet with a chemical shift of ~2.3 ppm, characteristic of a methyl group that is attached to a tertiary carbon. This provided further evidence for the presence of the branching unit in the oligomer.

DSC thermograms of the star-branched PPQs **16a–d** were obtained by heating the samples to 480°C at 20°C/min, quenching them to room temperature with liquid nitrogen, and then reheating, all in the DSC. The T_gs obtained during the initial heating ranged from 181 to 233°C, while the T_gs obtained during the reheating ranged from 259 to 284°C. The exotherm associated with the thermal polymerization of the phenylethynyl groups in **16a–d** began near 350°C and peaked above 400°C (Fig. 1, Table 4). Both the initial T_gs and the exothermic peak maxima increased with increasing $\bar{M}_n$, whereas the final T_gs decreased with increasing $\bar{M}_n$. The T_gs of analogous linear PPQs have been shown to increase as the molecular weight was increased in this region [12]. The exothermic peak, which can be attributed to chain extension of the terminal phenylethynyl groups, was shifted to higher temperatures as the $\bar{M}_n$ increased because the activation energy for the polymerization increased. The cured T_gs decreased as the $\bar{M}_n$ increased because the molecular weight between crosslinks increased.

In order to determine the processability of the oligomers, the melt viscosities of **16c** and **16d** were measured at 300°C with 2% strain in a RMS-800 rheometer using a dynamic mode on a parallel plate. As shown in Fig. 2, the melt viscosities of **16c** and **16d** were both dramatically lower than that of the linear PPQ prepared previously. The melt viscosity of **16c**(SPQ-46) was determined at NASA Langley on a RMS-4 rheometer at various temperatures with a fixed strain of 5% and a fixed angular frequency of 10 rad/sec. The melt viscosity of SPQ-46 decreased as the temperature was increased above 300°C and reached a minimum of 150 Pa sec at 348°C. Thus, the star-branched oligomers were expected to be readily melt processable.

*3.7. Properties of cured thin films of **16c,d***

To determine the properties of a cured system, thin films of **16d** were prepared from $CHCl_3$ solutions and then subjected to a series of heat treatments. The films were first heated in a vacuum oven to 180°C at approximately 20°C/min and maintained at this temperature for 24 h. Curing was then carried out at 350°C for varying periods of time in circulating air and in nitrogen. The cured films were cut into dumbbell specimen and tested according to ASTM D-882 (Table 5). The cured films had RT ultimate tensile strengths as high as 130 MPa and RT elongations at break of 30%. The tensile stength was significantly higher than that of the linear PPQ prepared in this study, which had RT tensile strength of 114 MPa. All the films were tough and flexible. They were insoluble in $CHCl_3$, THF, *m*-cresol, and NMP. The T_gs of the cured materials varied from 263 to 280°C depending on the curing atmosphere and the cure time. The lowest T_g was obtained when the curing was

Table 3
SEC analysis of star-branched PQ oligomers **16a–d**

Star-branched oligomer	Calcd. $\bar{M}_n$ (g/mol)	$\bar{M}_n$ (SEC) (g/mol)	$\bar{M}_w$ (SEC) (g/mol)	$\bar{M}_w/\bar{M}_n$ (SEC)
16a[a]	2924	2900	3520	1.21
16b[a]	4699	4190	5750	1.37
16c[a]	6475	5980	9510	1.59
16c(SPQ-46)[b]	6475	4816	8555	1.77
16d[c]	13,567	13,600	23,400	1.72

[a] SEC was performed in THF at 35°C.
[b] SEC was performed in NMP at 35°C at NASA-Langley.
[c] SEC was performed in $CHCl_3$ at 40°C.

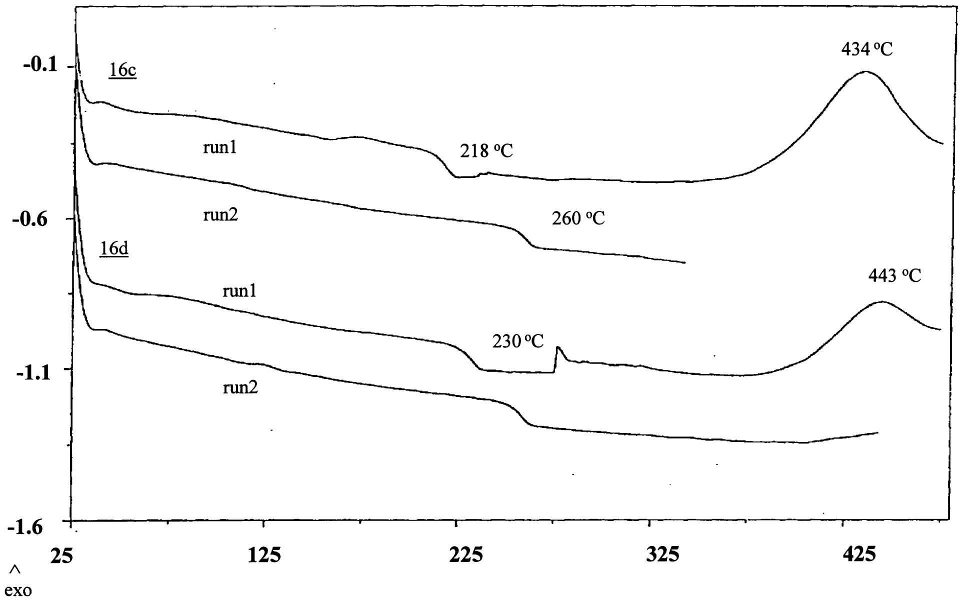

Fig. 1. DSC thermograms of oligomers **16c** and **16d**.

carried out in nitrogen for 2 h. In air, the T_g decreased as the curing time increased. These results suggest that an oxidative process also occurred in air that initially promoted crosslinking and then resulted in slight decomposition.

A thin film study was also conducted on **16c**(SPQ-46) at NASA Langley (Table 6). In this case, thin films were cast from NMP solutions and then heated 1 h at 100, 225 and 350°C, each in flowing air. The RT film moduli were more than twice those of the cured films of **16d**, while the elongations at break were approximately 1/5 those of **16d**. These results may be attributed to the $\bar{M}_n$ of **16c**(SPQ-46), which was approximately 1/3 that of **16d**. The lower $\bar{M}_n$ translates to a much higher crosslink density for **16c**.

The TGA thermograms of the cured films showed 5% weight losses between 544–557°C in nitrogen and between 544–570°C in air (Table 5). These results suggest that the cured oligomer has similar thermooxidative stability to the linear PPQ. To further investigate this phenomenon, both the cured oligomer samples and the linear PPQ were subjected to isothermal TGA analysis in a stream of air at 316°C. This test temperature is commonly used to evaluate the thermooxidative stability of conventional linear PPQs [35]. Both the linear PPQ and the cured star-branched oligomers displayed excellent weight retention under these test conditions. Both lost less than 1% of their weight after 1500 h at 316°C in circulating air.

*3.8. Adhesive properties of star-branched oligomer **16c**(SPQ-46)*

A preliminary evaluation of the adhesion of **16c**(SPQ-46) to titanium (Ti) was carried out. Thus, a standard glass supported adhesive film (tape) of the oligomer was prepared and pressed between two Ti (6Al-4V) adherends under 0.34 MPa compressive force with a final cure temperature of 350°C for 1 h. The single lap shear specimens, which had bondline thicknesses of about 0.010 cm, displayed disappointingly low tensile shear strengths of 17.8 MPa at 23°C and 20.0 MPa at 177°C, respectively. However, examination of the failed specimens revealed excessive distortion of

Table 4
Thermal properties of star-branched PQ oligomers **16a**–**d**

Star-branched oligomer	DSC (°C) Initial T_g[a]	Exothermic peak maximum	Final T_g[b]
16a	181	377, 419	284
16b	200	426	270
16c	218	434	260
16c(SPQ-46)	217	435	260
16d	233	443	259

[a] Inflection in baseline shift on DSC thermogram obtained in N_2 with a heating rate of 20°C/min.

[b] From second run on the sample that was quenched to room temperature with liquid N_2 after being heated to 480°C.

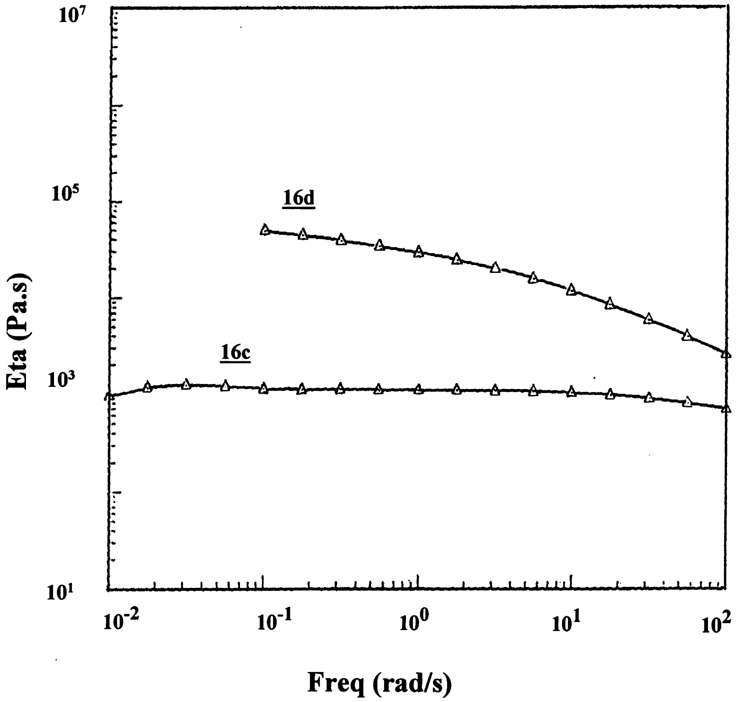

Fig. 2. Melt viscosities of star-branched PPQ oligomers **16c,d** vs frequency (measured at 300°C with 2% strain).

the glass carrier due to the high flow of the resin during fabrication. Additional specimens were then fabricated under contact pressure only with a final cure temperature of 350°C for 1 h. These samples, which had bondline thicknesses of about 0.013 cm, displayed significantly higher tensile shear strengths of 35.2 and 31.4 MPa at 23 and 177°C, respectively. Visual inspection indicated that the failure mode was predominantly cohesive.

*3.9. Properties of **16c**(SPQ-46)/carbon fiber (IM-7) composites*

A preliminary evaluation of the use of **16c**(SPQ-46) as a matrix resin in carbon fiber composites was carried out. Thus, unidirectional tape was prepared by coating unsized carbon fiber (IM-7) with an NMP solution of **16c**(SPQ-46) on a prepregging machine. Unidirectional laminates and laminates with 42/50/8 layups were fabricated in a vacuum press for flexural and open hole compression testing, respectively. The unidirectional laminates displayed excellent flexural strength and modulus (Table 7). The laminates also displayed very good retention of these flexural properties at 177°C. As a reference point, PETI-5/IM-7 laminates, display flexural strength and modulus at 33°C of 1788 MPa and 1.45 GPa, respectively [36]. PETI-5 is a phenylethynyl-terminated imide oligomer with a $\bar{M}_n$ of about 5000 that has been selected as the baseline material for the United States high speed civil transport program [37]. The open hole compressive strengths of the **16c**(SPQ-46)/IM-7 composites were also excellent (Table 7). In fact, these results were somewhat surprising because the tensile moduli of thin films of **16c**(SPQ-46) were relatively low. Generally, matrix resins with moduli below about 3.1 GPa do not provide high compressive properties, because the matrix has inadequate stiffness to prevent the fiber from micro-buckling [38].

Table 5
Properties of cured samples of star-branched PQ oligomer **16d**

Curing conditions	Film[a] properties	T_g[b]	TGA[c] (°C)		Tensile[d] properties		
			N_2	Air	Ultimate tensile strength (MPa)	Elongation at break (%)	Young's modulus (MPa)
350°C /air/0.5 h	Tough and flexible	280	544	544	130	29	939
350°C /air/1.0 h	Tough and flexible	272	557	565	122	30	938
350°C /N_2/2.0 h	Tough and flexible	263	556	570	125	28	1031

[a] Cast from 10% (w/v) chloroform solutions.

[b] Inflection in baseline shift on DSC thermogram obtained in N_2 with a heating rate of 20°C/min.

[c] Temperature at which 5% weight loss occurred on TGA thermogram with a heating rate of 10°C/min.

[d] Determined on thin films according to ASTM D-882.

Table 6
Thin film tensile properties of cured **16c**(SPQ-46)

Test condition (°C)	Ultimate[a] tensile strength (MPa)	Young's modulus (MPa)	Elongation at break (%)
23	100	2358	5.9
177	60.7	2033	3.8

[a] Tensile properties were determined according to ASTM D-882 using four specimens per test condition.
(Films were cast from a 30% (wt/wt) NMP solution on dry plate glass and cured by heating for 1 h at 100, 225 and 350°C each in flowing air).

Table 7
Preliminary properties of **16c**(SPQ-46)/IM-7 composites (NA—not available)

Test	Test condition (°C)	Strength (MPa)	Modulus (GPa)
Flexural	23	1902	1.38
	177	1503	1.37
Open hole compressive strength	23	433	NA
	177	315	NA

4. Summary and conclusions

Several phenylethynyl-terminated, star-branched PQ oligomers have been prepared with $\bar{M}_n$s that range from 2900 to 13,600 g/mol (SEC). The amorphous oligomers can be readily solution processed due to their high solubility in common organic solvents or melt processed due to their low melt viscosities. Due to their relatively low T_gs (181–233°C), melt processing can be carried out at temperatures considerably below their cure temperature (350°C). The cured resins display excellent solvent resistance, elevated T_gs (259–284°C), and thermooxidative stability very similar to that of linear PPQs.

One of the oligomers (SPQ-46) with an $\bar{M}_n$ of 4816 g/mol (SEC) has been used to prepare thin films, titanium lap shear adhesive specimens, and carbon fiber (IM-7) composites for testing. The cured thin films displayed an average room temperature (RT) tensile strength of 100 MPa, a RT modulus of 2358 MPa, and a RT elongation of 5.9%. The cured adhesive specimens gave a titanium–titanium lap shear strength of 35.2 MPa at RT. The cured oligomer showed good retention of its thin film and adhesive properties at 177°C. The SPQ-46/IM-7 composite samples displayed a flexural strength of 1902 MPa, a modulus of 1.38 GPa and an open hole compressive strength of 433 MPa. These values are very similar to those displayed by the current state-of-the-art PETI-5/IM-7 composites being developed for use on the US high speed civil transport. The results of this study suggest that the oligomers are excellent candidates for composite fabrication via resin transfer molding (RTM) and resin infusion processes.

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