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## Polyquinoxaline Matrix Resins And Composites

Paul M. Hergenrother

*NASA Langley Research*, p.m.hergenrother@larc.nasa.gov

John W. Connell

*NASA Langley Research*, j.w.connell@larc.nasa.gov

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## POLYQUINOXALINE MATRIX RESINS AND COMPOSITES

PAUL M. HERGENROTHER  
AND JOHN W. CONNELL  
NASA Langley Research  
Center, Langley Blvd  
Hampton, VA

Polyquinoxalines (PQs) are heterocyclic polymers that contain the heteroaromatic benzo [ $\alpha$ ] pyrazine (quinoxaline) ring along the main chain. The polymers may be unsubstituted or contain pendent substituents such as phenyl groups on the quinoxaline ring. Quinoxaline polymers are generally synthesized from the step-growth polymerization of aromatic bis(*o*-diamines) and bis( $\alpha$ -dicarbonyl) compounds. This synthetic route to PQs was proposed in 1961 [1], and the first synthesis was reported in 1964 [2,3]. Polyphenylquinoxalines (PPQs) were first reported in 1967 [4]. Recently, PPQs have been prepared by an aromatic nucleophilic displacement route [5,6]. Review articles concerning the synthesis, characterization, and properties of PQs are available [7–9].

The properties of the PQs can be altered by changing the chemical structure of the polymer backbone and also the chemical nature of the pendent group on the quinoxaline ring. This unique feature provides versatility in designing PQs with an attractive combination of properties for use in specific applications. Variations of quinoxaline polymers include copolymers and oligomers end-capped with reactive groups such as vinyl, ethynyl, and phenylethynyl.

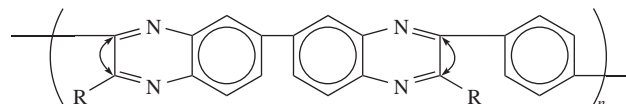
A unique feature of linear PQs is their excellent solubility in the fully cyclized form. Unlike most other aromatic heterocyclic polymers, high molecular weight PQs form solutions that can be used in a variety of applications to form films, ultrafiltration membranes, bioreactor cells, and protective coatings, as well as to impregnate reinforcements. PQs are an important family of polymers that offer high chemical and thermal stability coupled with high mechanical properties. They are potentially useful as functional resins (e.g., films and coatings) and structural resins (e.g., adhesives and composite matrices) in many applications that demand stability in harsh environments. This article reviews some neat resin properties with emphasis on the use of PQs as matrix resins in fiber-reinforced composites.

### POLYMER PROPERTIES

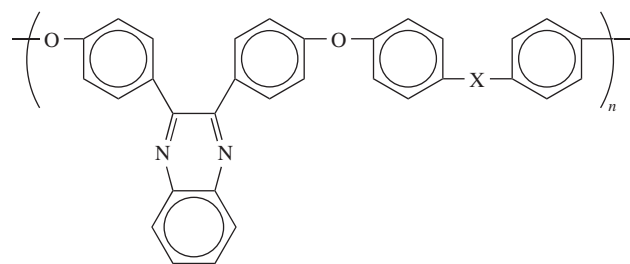
#### Glass-Transition Temperatures

The very rigid PQ (1) [10], PPQ (2) [11], and PPQ (3) [5] have been reported to display some crystalline character

by differential scanning calorimetry (DSC) and wide-angle X-ray diffraction (WAXS) studies. However, the vast majority of quinoxaline polymers show no crystallinity by DSC or WAXS studies.



where (1) R = H and (2) R = C<sub>6</sub>H<sub>5</sub>



where (3) X = 1,4-COC<sub>6</sub>H<sub>4</sub>CO.

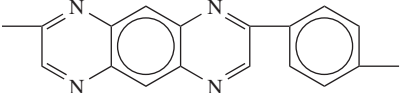
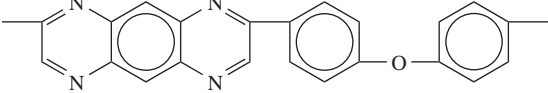
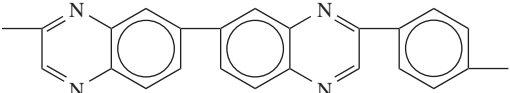
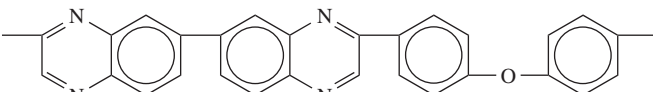
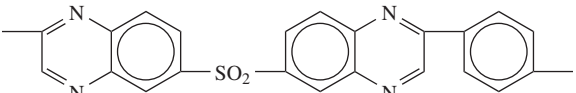
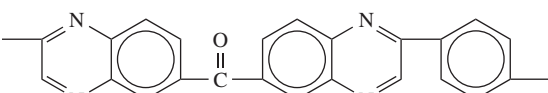
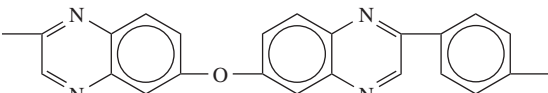
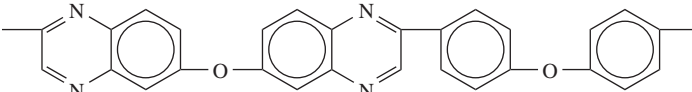
Their amorphous nature is due to the configurational disorder (isomers) in the backbone of the polymer chains, as represented by the double-headed arrows of (1) and (2); PPQ (3) has no configurational isomers. The glass-transition temperatures ( $T_g$ s) of PQs and PPQs are controlled primarily by the chemical structure, molecular weight, and thermal history. Discretion is advised when comparing the  $T_g$ s of polymers prepared in different laboratories and determined by different methods, or by the same method but under different conditions (e.g., heating rate, load, and frequency).

The  $T_g$ s of the PQs listed in Table 1 range from a high of 393°C for a rigid PQ to a low of 261°C for a flexible PQ containing diphenyl ether units. Table 2 shows the  $T_g$ s for representative PPQs, ranging from 213 to 370°C for the all-aromatic polymers. The  $T_g$ s of PPQs without configurational isomers (Connell and Hergenrother, unpublished data) [5], prepared by aromatic nucleophilic substitution, are shown in Table 3. In several cases, crystallinity was determined by WAXS and melting endotherms detected by DSC. Table 4 lists  $T_g$ s of some aryl-ether-containing PPQs prepared by aromatic nucleophilic substitution [6]. The  $T_g$ s of PPQs containing nonreactive substituents on the pendent phenyl group appear in Table 5. The PPQ containing a 4-hydroxy substituent has the highest  $T_g$  as a result of intermolecular hydrogen bonding. Table 6 shows the  $T_g$ s of PPQ copolymers containing imide, amide, and ester moieties. Other copolymers containing phenylquinoxaline and imide units were recently reported [12].

PPQs are high temperature thermoplastics that generally exhibit a large window between the  $T_g$  and the decomposition temperature, making them attractive for processing. However, their thermoplastic nature makes them subject to thermoplastic failure near  $T_g$  and poten-

Adapted from *Polyquinoxaline Matrix Resins and Composites*, First Edition.

**Table 1. Apparent Glass-Transition Temperatures of Polyquinoxalines**

Repeat Unit <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	Reference
	393	[13]
	354	[13]
	376	[13]
	305 280 <sup>c</sup>	[13] [14]
	342	[13]
	318	[13]
	306	[13]
	261	Hergenrother, unpublished data.

<sup>a</sup>Only one isomer is shown.<sup>b</sup>Determined by DSC at a heating rate of 20°C/min unless otherwise stated.<sup>c</sup>Determined by dielectric measurements.

tial creep problems below  $T_g$  while under load. In attempts to increase  $T_g$ , reactive groups have been placed on the pendent phenyl group for subsequent thermal reactions. Table 7 lists the initial and cured  $T_g$ s for several PPQs containing reactive substituents on the pendent phenyl group. Cure conditions vary from 0.5 h at 350°C in nitrogen to 1 min or less at temperatures as high as 475°C in nitrogen. Organic polymers undergo some decomposition when heated to temperatures as high as 475°C, even in a nitrogen atmosphere.

Other routes have been investigated to increase the  $T_g$  and also to improve the processability of PPQ. Acetylene-

terminated phenylquinoxaline oligomers (ATPQ) have been reported [32–34]. At elevated temperatures, the terminal acetylenic group undergoes a complex reaction that leads to chain extension and cross-linking.

#### Thermal Stability

The thermal stability of quinoxaline polymers has been determined by thermogravimetric analysis (TGA), isothermogravimetric analysis (ITGA), and the retention of mechanical properties at elevated temperatures after exposure for various times at elevated temperatures. TGA of analogous PQs and PPQs seems to indicate

**Table 2. Apparent Glass-Transition Temperatures of Polyphenylquinoxalines**

$X^a$	R	$\eta_{inh}$ (dL/g) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>	Reference
Nil	—(CF <sub>2</sub> ) <sub>4</sub> —	0.39	207	[15]
Nil		0.93	220	[16]
Nil		0.48 <sup>d</sup>	316	(Harris and Hergenrother, private communication)
Nil		0.65 <sup>d</sup>	390	(Harris and Hergenrother, private communication)
Nil		2.4	370	[17]
Nil		1.3	320	[18]
Nil		1.2	290	[19]
Nil		0.83	283	[5]
Nil		0.77	261	[20]
Nil		0.75	257	[20]

*(continued overleaf)*

Table 2. (continued)

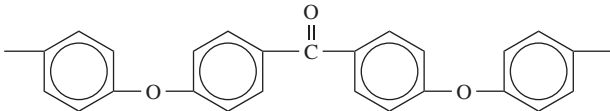
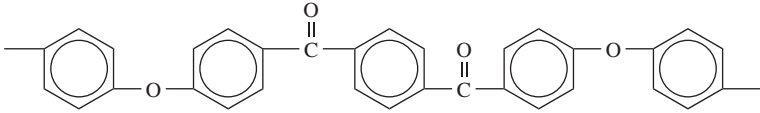
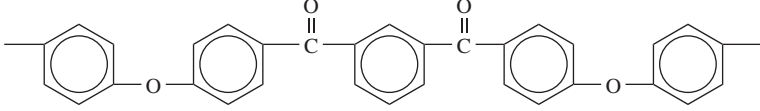
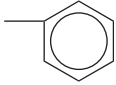

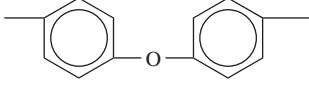
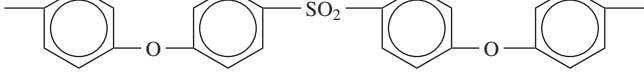
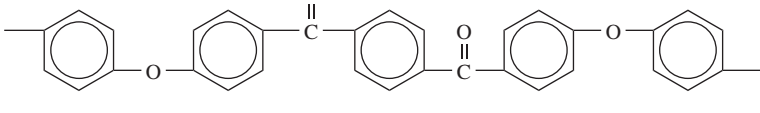
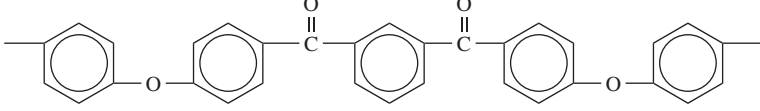



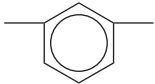

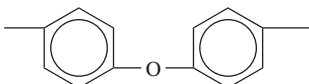
$X^a$	R	$\eta_{inh}$ (dL/g) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>	Reference
Nil		0.80	252	[5]
Nil		1.29 <sup>e</sup>	252	[21]
Nil		1.09 1.01 <sup>e</sup>	240 239	[5] [21]
O		1.7	298	[22]
O		1.9	279	[22]
O		2.1	257	[22]
O		0.34	240	[5]
O		1.78 <sup>e</sup> 0.45	232 226	[21] [5]
—		1.12 <sup>e</sup> 0.46	221 213	[21] [5]
		2.3	325	[22]
		1.3	288	[22]
		1.5	269	[22]

Table 2. (continued)

X <sup>a</sup>	R	$\eta_{\text{inh}}$ (dL/g) <sup>b</sup>	T <sub>g</sub> (°C) <sup>c</sup>	Reference
		0.69	268	[5]
		0.56 <sup>d</sup>	263	[23]
		1.01	255	[5]
		1.30	253	[5]
		0.68 <sup>d</sup>	249	[23]
		0.61 1.02 <sup>e</sup>	235 234	[5] [21]
SO <sub>2</sub>		1.8	346	[22]
SO <sub>2</sub>		1.4	324	[22]
SO <sub>2</sub>		1.5	293	[22]

<sup>a</sup>When X is nil, the phenyl rings are directly joined.

<sup>b</sup>Inherent viscosity of 0.5% *m*-cresol solution at 25°C unless otherwise stated.

<sup>c</sup>By DSC at a heating rate of 20°C/min.

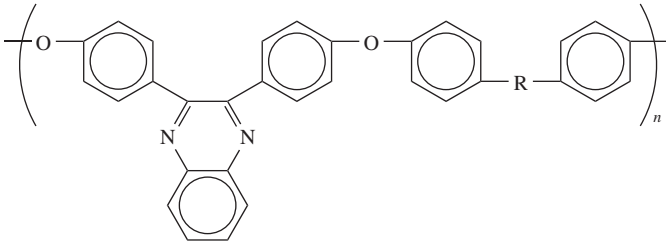

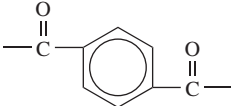
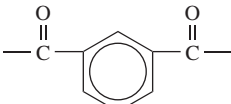
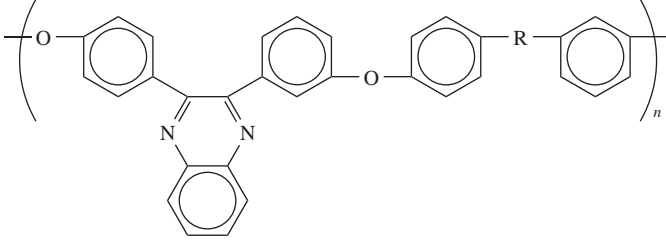
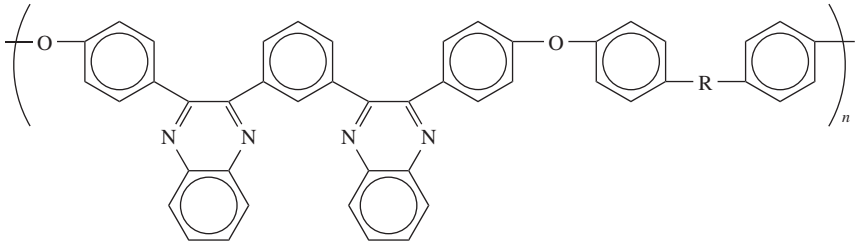
<sup>d</sup>Inherent viscosity of 0.5% *sym*-tetrachloroethane solution at 35°C.

<sup>e</sup>Inherent viscosity of 0.5% chloroform solution at 25°C.

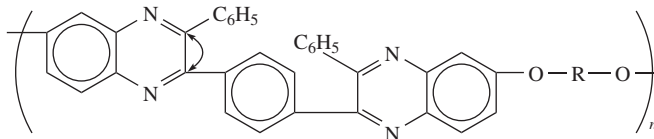
similar thermal stabilities, but ITGA shows the PPQs to be significantly more stable than the PQs. This was first observed in 1967 [4], and since then several studies have been conducted to demonstrate the superior thermo-oxidative stability of PPQs over PQs. For a more thorough discussion on the thermal stability of PQs and

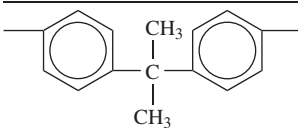
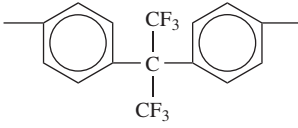
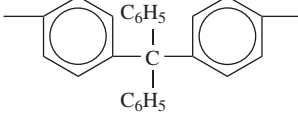
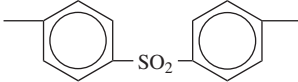
PPQs, the reader is directed to Ref. 8. In addition to their excellent thermal stability, PPQs exhibit outstanding stability to strong bases and acids. For example, PPQs are unchanged after refluxing them in 40% aqueous potassium hydroxide for 6 h [4]. Equally good stability has also been shown toward hot acids. Small composite

Table 3. Apparent Glass-Transition Temperatures of Polyphenylquinoxalines

R	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	$T_g$ (°C) <sup>b</sup>	Reference <sup>c</sup>
	0.54	240	[5]
	0.58	209	[5]
	0.83	208 (365) <sup>d</sup>	[5]
	0.50	179	[5]
	0.52	179 (377) <sup>d</sup>	[24]
	0.24	235 (388) <sup>d</sup>	(Connell and Hergenrother, unpublished data)

<sup>a</sup>Inherent viscosity of 0.5% *m*-cresol solution at 25°C.<sup>b</sup>Determined by DSC at a heating rate of 20°C/min.<sup>c</sup>All polymers precipitated during synthesis, thereby limiting molecular weight.<sup>d</sup>Denotes crystalline melt temperature.

**Table 4. Apparent Glass-Transition Temperatures of Polyphenylquinoxalines**


R	$\eta_{\text{inh}}$ (dL/g) <sup>a</sup>	$T_g$ (°C) <sup>b</sup>
	1.20	255
	1.20	255
	1.45	270
	0.55	285

<sup>a</sup>Intrinsic viscosity in *N*-methylpyrrolidone at 25°C.

<sup>b</sup>Determined by DSC at a heating rate of 10°C/min.

Source: From Ref. 6.

nozzles of PPQs have shown excellent stability on deep submergence in geothermal energy wells (superheated steam, brine, and sulfur compounds). Thin-film coatings (~0.0025-mm thick) applied to aluminum by spray coating protected the metal from the corrosive environment [22].

## MECHANICAL PROPERTIES

### Films

Films of linear PQs and PPQs can be prepared by melt pressing at temperatures above the  $T_g$  or, preferably, by solution casting. Solutions at concentrations of 10–20% solids in solvents, such as chloroform, *sym*-tetrachloroethane, *m*-cresol, and mixtures of *m*-cresol with xylene or toluene, can be readily used to prepare films. The solution is cast onto an appropriate substrate (e.g., plate glass) and the solvent removed by careful heating to avoid bubbles. When casting from an *m*-cresol solution, the film should be heated above the  $T_g$  of the polymer to ensure complete solvent removal. Quinoxaline polymers hold small amounts (e.g., ~1%) of *m*-cresol very tenaciously. Films as thick as 0.2 mm have been prepared by solution casting. Little work has been done with PQ

films, whereas the film properties of many structurally different PPQs have been determined (Table 8). The film properties were obtained without optimization or orientation.

Thin films (0.05 mm-thick, cured for 1 h at 300°C in vacuum) of a PQ gave at 25 and 177°C tensile strengths (ASTM D882) of 124.1 and 96.5 MPa, tensile moduli of 2.76 and 1.93 GPa, and ultimate elongation of 4.5 and 21.0%, respectively [7]. The thin-film properties vary as a function of the chemical structure of the polymer, molecular weight, quality of the film, and film drying conditions. PPQ films containing 5 and 10 mol% pendent phenylethynyl groups undergo cross-linking at elevated temperatures to provide lower elongations, higher  $T_g$ s, and better retention of properties at high temperatures.

### Fracture Energy

The fracture toughness ( $K_{Ic}$ , stress intensity factor; or  $G_{Ic}$ , critical strain energy release rate) for PQs has not been reported. PPQs are very tough materials, as evidenced by the room temperature  $G_{Ic}$  as determined by ASTM E399 on compact tension specimens (Table 9). The fractured surface of the last three PPQs [21] in Table 9 showed tremendous crazing, creating new surface area, which is



**Table 5. Apparent Glass-Transition Temperatures of Polyphenylquinoxalines Containing Nonreactive Substituents on the Pendent Phenyl Group**

$X^b$	Y	$\eta_{inh}$ (dL/g) <sup>c</sup>	$T_g$ (°C) <sup>d</sup>	Reference
Nil		0.57	353 <sup>f</sup>	[25]
Nil		0.64	288	[19]
Nil		0.64	306	[19]
Nil		1.10 <sup>g</sup>	375	[19]
Nil		0.45	245	[19]
Nil		0.81	326	[19]
Nil		0.52	282	[26]
Nil		0.51	289	[26]
Nil		1.10	313	[19]
		0.72	215	[27]

Table 5. (continued)

X <sup>b</sup>	Y	$\eta_{\text{inh}}$ (dL/g) <sup>c</sup>	$T_g$ (°C) <sup>d</sup>	Reference
		0.62	206	[27]
		0.61	200	[27]

<sup>a</sup>Ar is *m*-substituted phenyl unless otherwise stated.

<sup>b</sup>When X is nil, the phenyl rings are directly joined.

<sup>c</sup>Inherent viscosity of 0.5% *m*-cresol solution at 25°C.

<sup>d</sup>By DSC at a heating rate of 20°C/min.

<sup>e</sup>Ar = *p*-substituted phenyl .

<sup>f</sup>By torsional braid analysis at a heating rate of 4.2°C/min.

<sup>g</sup>Inherent viscosity of 0.5% *N,N*-dimethylacetamide solution at 25°C.

<sup>h</sup>Ar = 4,4'-diphenyl ether .

a mechanism for energy dissipation often seen in tough thermoplastics.

### Adhesives

Linear PQs and PPQs are excellent high temperature adhesives for joining plastic, ceramic, composite, and metal to themselves and to each other. They are generally processed at temperatures above their  $T_g$  under low to moderate pressure. Adhesive work with PPQs has been more extensive than with PQs. A complete discussion of the adhesive properties of PQs and PPQs is beyond the scope of this article, and the reader is directed to Ref. 8.

### Composites

PQs and PPQs have undergone preliminary evaluation as composite matrixes using glass [38], different types of carbon-graphite [7,17,22,24,35,39–43], and boron [38,40] filament reinforcements. When comparing the properties of different laminates, factors such as the type of fiber, surface treatment, sizing, prepreg quality, and process conditions are important. The early carbon-graphite composite work with quinoxaline polymers and other temperature polymers is difficult to evaluate because the properties (e.g., tensile strength and thermo-oxidative stability) of the various fibers, and of different batches of the same fiber as well, differed significantly. In addition, various fibers often contained contaminants (e.g., residual metal, such as sodium), and these contaminants catalyzed the degradation of the matrix under thermo-oxidative conditions.

Fabric or unidirectional PQ and PPQ prepreps are generally prepared by multiple solution coating. The prepreg can be dried to low volatile content (e.g., <1%), and the board prepreg subsequently laid up and fabricated into composites, using temperatures greater than the  $T_g$  of

the polymer under moderate pressure. Even at temperatures above the  $T_g$  of a PQ or PPQ, the melt viscosity is very high, which causes problems in accommodating the escape of residual volatiles and even trapped air in compression and injection molding operations. Little work has been directed toward controlling the molecular weight and end-capping PPQ to lower the melt viscosity and improve melt stability.

Glass, boron, and carbon-graphite (Modmore ||) filament-reinforced laminate properties of the PQ are presented in Tables 10 and 11. This work was directed toward the development of composites that would exhibit useful mechanical properties at >300°C. Table 11 shows that PQ carbon-graphite composites exhibit excellent retention of mechanical properties at 315°C after 200 h at 315°C in air, and at 371°C after 50 h in air.

PPQ composites have been fabricated from carbon-graphite filament reinforcements impregnated with high molecular weight polymer or oligomeric material. Solutions of high molecular weight PPQs are relatively viscous, and therefore thorough wetting of the fiber bundles is difficult. Solutions of PPQ monomers or oligomeric forms are of low viscosity, which permits better wetting of the fibers. Properties of carbon-graphite unidirectional composites of a PPQ are presented in Table 12. The initial  $T_g$  of this PPQ was 285°C. After fabrication of the composite at temperatures to 429°C, the  $T_g$  of the polymer increased, presumably due to cross-linking, resulting in usable properties at 316°C. The unidirectional composite properties of a different PPQ are presented in Table 13. A monomeric or oligomeric solution was used to impregnate the carbon-graphite fiber. The room-temperature flexural modulus of 142.7 GPa is quite respectable, and the transverse tensile strength of 80 MPa is significantly higher than that of state-of-the-art

**Table 6. Apparent Glass-Transition Temperatures of Phenylquinoxaline Copolymers**

X	Ar	$\eta_{inh}$ (dL/g)	$T_g$ ( $^{\circ}$ C)	Reference
Nil		1.54 <sup>a</sup>	260 <sup>b</sup>	[28]
Nil		1.85 <sup>a</sup>	279 <sup>b</sup>	[29]
Nil		1.96 <sup>c</sup>	187 <sup>d</sup>	[26]
Nil		2.17 <sup>c</sup>	296 <sup>d</sup>	[26]
Nil		1.05 <sup>c</sup>	298 <sup>d</sup>	[26]
0		1.09 <sup>a</sup>	254 <sup>b</sup>	[28]
0		1.32 <sup>a</sup>	298 <sup>b</sup>	[29]
0		1.04 <sup>a</sup>	266 <sup>b</sup>	[29]

<sup>a</sup>Inherent viscosity of 0.5% *m*-cresol solution at 30 $^{\circ}$ C.<sup>b</sup>Determined by dielectric measurements at a heating rate of 5 $^{\circ}$ C/min.<sup>c</sup>Inherent viscosity of 0.5% *m*-cresol solution at 25 $^{\circ}$ C.<sup>d</sup>Determined by DSC at a heating rate of 20 $^{\circ}$ C/min.

**Table 7. Apparent Glass-Transition Temperatures of Polyphenylquinoxalines Containing Reactive Substituents on the Pendent Phenyl Group**

$X^a$	Ar	Y	$\eta_{\text{inh}}$ (dL/g) <sup>b</sup>	$T_g$ (°C) <sup>c</sup>		Reference
				Initial	Cured	
Nil		—OCN	1.17	ND <sup>d</sup>	ND	[19]
Nil			0.51	227	327	[19]
Nil		—CH <sub>3</sub>	0.57 <sup>e</sup>	353 <sup>f</sup>	440 <sup>f</sup>	[25]
Nil		—CN	1.62	340	371	[19]
Nil		—C≡CH	1.23	ND	ND	[30]
Nil		—C≡CC <sub>6</sub> H <sub>5</sub>	1.05	325	ND	[31]
Nil			0.47	ND	ND	[30]
Nil			0.43	231	ND	[31]
			0.51	227	327	[19]
Nil		—C≡CC <sub>6</sub> H <sub>5</sub>	0.82	253	ND	Hergenrother, unpublished data.

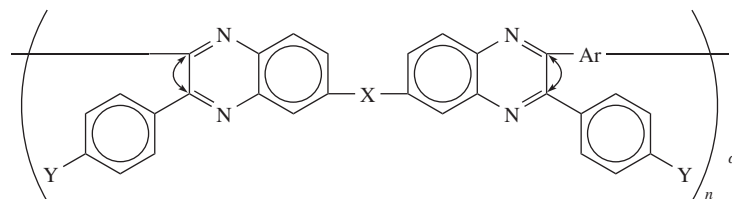
<sup>a</sup>When X is nil, the phenyl rings are directly joined.<sup>b</sup>Inherent viscosity of 0.5% *m*-cresol solution at 25°C.<sup>c</sup>Determined by DSC at a heating rate of 20°C/min.<sup>d</sup>ND = not detected.<sup>e</sup>Intrinsic viscosity in *m*-cresol at 30°C.<sup>f</sup>Determined by torsional braid analysis at a heating rate of 4.2°C/min.

Table 8. Thin-Film Properties of Polyphenylquinoxalines

$X^b$	Ar	$T_g$ (°C) <sup>c</sup>	Test Temperature (°C)	Tensile Strength (MPa) <sup>d</sup>	Tensile Modulus (GPa) <sup>d</sup>	Break Elongation (%)	Reference
Nil		290	25	117.2	2.76	23.0	Hergenrother, unpublished data.
			177	65.5	2.28	51.0	
			232	35.8	1.67	83.0	
Nil		357	25 232	127.5 87.6	2.83 1.70	7.1 12.9	[20]
Nil		394	25 232	122.7 100.0	3.10 2.34	4.8 8.2	[20]
O		261	25 200 232	111.0 50.3 29.3	2.44 1.64 1.37	7.1 12.3 24.0	[35]
O		277	25 200 232	111.0 56.5 48.0	2.57 1.78 1.76	6.2 10.7 14.5	[35]
O		—	25	124.8		128.0	[36]
Nil		—	25 150 300	115.7 62.0 34.3	2.04 1.54 0.68	9.1 46.0 153.0	[37]

(continued overleaf)

(continued)



$X^b$	Ar	$T_g$ (°C) <sup>c</sup>	Test Temperature (°C)	Tensile Strength (MPa) <sup>d</sup>	Tensile Modulus (GPa) <sup>d</sup>	Break Elongation (%)	Reference
Nil		—	25 200 300	117.6 81.3 49	2.11 1.57 1.08	9.5 62.0 116.0	[37]
Nil		220	25 93	99.3 68.9	2.61 2.01	8.1 10.5	[16]
Nil		239	25 177	108.3 48.0	3.26 2.08	6.5 60.3	[21]
Nil		252	25 177	93.8 57.6	2.73 2.42	8.6 38.5	[21]
O		221	25 177	95.8 47.5	3.13 2.37	5.3 31.9	[21]

<sup>a</sup>Y = H unless otherwise stated.

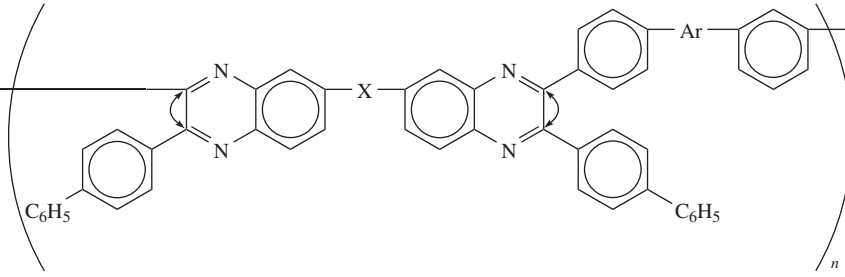
<sup>b</sup>When X is nil, the phenyl rings are directly joined.

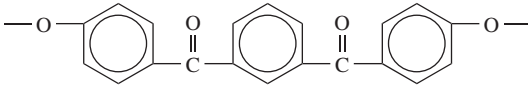
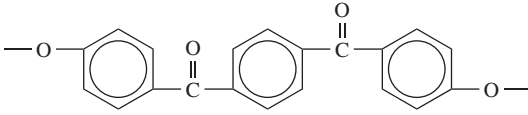
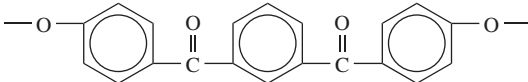
<sup>c</sup>Determined by DSC at a heating rate of 20°C/min.

<sup>d</sup>ASTM D882.

<sup>e</sup>Y = 90% H, 10% C≡CC<sub>6</sub>H<sub>5</sub>.

<sup>f</sup>Y = 95%, 5% C≡CC<sub>6</sub>H<sub>5</sub>.

**Table 9. Fracture Toughness of Polyphenylquinoxalines**


$X^a$	Ar	Fracture Toughness $G_{IC}$ ( $J/m^2$ )	Reference
Nil	—O—	2555	[16]
Nil	—O—(CH <sub>2</sub> ) <sub>3</sub> —O—	945	[16]
Nil	—O—(CH <sub>2</sub> ) <sub>4</sub> —O—	1452	[16]
Nil	—O—(CH <sub>2</sub> ) <sub>5</sub> —O—	1837	[16]
Nil	—O—(CH <sub>2</sub> ) <sub>6</sub> —O—	1837	[16]
Nil		4235	[21]
Nil		2485	[21]
O		4392	[21]

<sup>a</sup>When X is nil, the phenyl rings are directly joined.

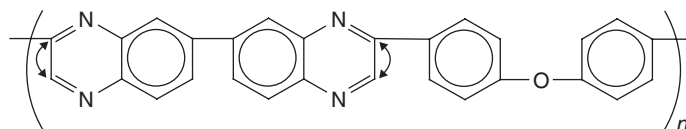
<sup>b</sup>Tested at room temperature according to ASTM E399, average of four specimens per test condition.

epoxy composites [42]. The unidirectional composite properties of an acetylene-terminated phenylquinoxaline oligomer are presented in Table 14. This material showed excellent retention of room-temperature properties when tested at 232°C before and after isothermal caging at 232°C. Preliminary studies of composite properties for a PPQ containing 5 mol% of pendent phenylethynyl groups showed better retention of properties at elevated

temperatures than for an analogous PPQ without the pendent phenylethynyl groups [35].

## CONCLUSIONS

PQs and PPQs are a family of high performance, high temperature polymers that have potential use in functional and structural applications. One PPQ is presently

**Table 10. Polyquinoxaline Laminate Properties**

Test Condition	Flexural Strength (GPa) <sup>a</sup>	Flexural Modulus (GPa) <sup>a</sup>
PQ glass <sup>b</sup> laminate <sup>c</sup>		
25°C	0.687	25.1
371°C after 1 h at 371°C	0.425	16.8
371°C after 50 h at 371°C	0.303	17.3
538°C after 10 min at 538°C	0.117	15.1
PQ boron unidirectional laminate <sup>d,e</sup>		
25°C	1.74	291.6
316°C after 10 min at 316°C	1.52	166.8
316°C after 10 min at 361°C	1.66	83.4

<sup>a</sup>ASTM D790.

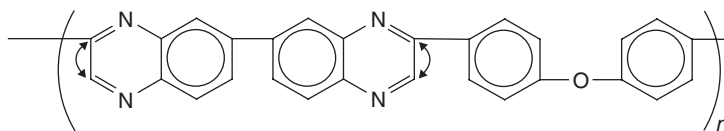
<sup>b</sup>1581 style AF-994 glass fabric with a HT-S finish.

<sup>c</sup>Press cured for 10 min at 232°C under 1.4 MPa, followed by postcure unrestrained of 4 h each at 205 and 232°C, 8 h at 288°C, 4 h each at 316 and 344°C, and 8 h at 371°C under a nitrogen atmosphere. Resin content, 33.1%; density, 1.71 g/cm<sup>3</sup>; and calculated void content, 8.6%.

<sup>d</sup>Tungsten core; filaments, ~0.01 cm thick; tensile strength, ~0.345 GPa; and tensile modulus, ~386.1 GPa.

<sup>e</sup>Press cured by 5 min contact at 382–394°C, then 4 h at 394°C under 3.4 MPa; postcured same as reported in footnote *d*.

Source: From Ref. 38.

**Table 11. Polyquinoxaline Modmor II Unidirectional Laminate Properties<sup>a,b</sup>**

Test Condition	Flexural Strength (GPa) <sup>c</sup>	Flexural Modulus (GPa) <sup>c</sup>	Short-Beam Shear Strength (MPa) <sup>d</sup>
25°C	0.842	106.9	88.2
315°C after 1 h at 315°C, air	0.815	104.8	59.3
315°C after 200 h at 315°C, air	0.650	100.6	48.3
371°C after 1 h at 371°C, air	0.747	104.1	61.4
371°C after 50 h at 371°C, air	0.713	100.0	60.7

<sup>a</sup>Tensile strength, ~2.41 GPa; tensile modulus, ~262.0 GPa; and density, 1.71 g/cm<sup>3</sup>.

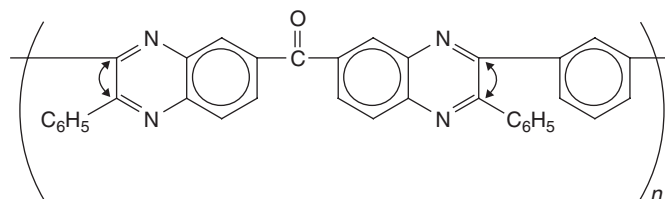
<sup>b</sup>Resin content, 34.3%; density, 1.50 g/cm<sup>3</sup>; and calculated void content, 4.3%. Press cured at 232°C for 10 min, 316°C for 2 h with intermittent bumping, and 395°C for 1 h under 1.7 MPa; postcured through 4 h at 395°C in a nitrogen atmosphere unrestrained. Tensile strength, 0.887 GPa; tensile modulus, 131.7 GPa. Compression strength, 0.512 GPa; compression modulus, 102.0 GPa.

<sup>c</sup>ASTM D790.

<sup>d</sup>ASTM D2344.

Source: From Ref. 7.



**Table 12. Polyphenylquinoxaline Unidirectional Carbon-Graphite Laminate Properties<sup>a</sup>**

Fiber	Prepreg	Resin Content (%) <sup>b</sup>	Average Flexural Strength (GPa) <sup>c</sup>	Flexural Modulus (GPa) <sup>c</sup>	Interlaminar Shear Strength (MPa) <sup>d</sup>
Hercules HM-S <sup>e</sup> 25°C	32% Resin, 0.3% volatiles	30	0.841	103.4	42.7
316°C after 10 min at 316°C			0.385	57.2	23.4
316°C after 500 h at 316°C			0.338	27.6	24.8
Hercules HT-S <sup>f</sup> 25°C	34% Resin, 0.18% volatiles	32	1.379	148.9	62.7
316°C after 10 min at 316°C			0.944	135.1	57.2

<sup>a</sup>Tests in air. Cure conditions: 1 h at 339°C; 2 h at 429°C under 0.69 MPa.

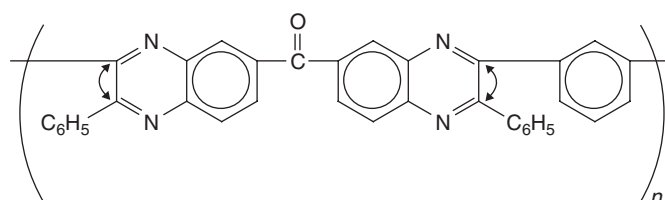
<sup>b</sup>Calculated.

<sup>c</sup>ASTM D790.

<sup>d</sup>ASTM D2344.

<sup>e</sup>Tensile strength, ~2.275 GPa; tensile modulus, ~351.6 GPa; density, ~1.83 g/cm<sup>3</sup>; and elongation, ~0.58%.

<sup>f</sup>Tensile strength, ~2.895 GPa; tensile modulus, ~255.1 GPa; density, ~1.66 g/cm<sup>3</sup>; and elongation, ~1.1%.

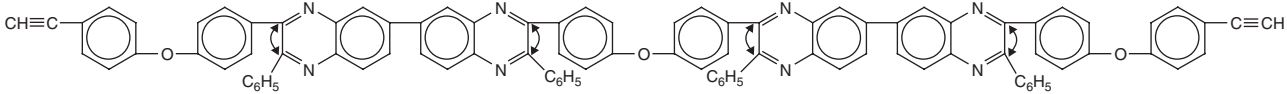
**Table 13. Polyphenylquinoxaline Unidirectional Carbon-Graphite Laminate Properties<sup>a</sup>**

Fiber	Flexural Strength (GPa) <sup>b</sup>	Flexural Modulus (GPa) <sup>b</sup>	Interlaminar Shear Strength (MPa) <sup>b</sup>	Reference
Hercules HM-S <sup>b</sup> 25°C	0.848	142.7	52.4	[41]
316°C	0.483	70.3	29.3	—
Hercules HT-S <sup>b,c</sup> 25°C	1.289	—	103.4	[42]

<sup>a</sup>Cure conditions: 1 h each at 329, 329, and 371°C under 6.2 MPa; extended postcure unrestrained for 2 h each at 25°C increments.

<sup>b</sup>See Table 14.

<sup>c</sup>Transverse tensile strength, 80.0 MPa (ASTM D3339-76).

**Table 14. Acetylene-Terminated Phenylquinoxaline Unidirectional HT-S Laminate Properties<sup>a</sup>**


Cure Conditions	25 °C	232 °C after 10 min at 232 °C	232 °C after 30 d at 71 °C, 95% RH	232 °C after 2000 h at 232 °C, air	260 °C after 10 min at 260 °C, air	260 °C after 500 h at 260 °C, air	Reference
2 h at 288 °C under 1.4 MPa, 16 h at 316 °C unrestrained							
Flexural strength, GPa <sup>b</sup>	0.152	—	0.137	—	0.134	—	[44]
Flexural modulus, GPa <sup>b</sup>	134	—	132	—	125	—	
Interlaminar shear strength, MPa <sup>c</sup>	103	—	—	—	—	—	
4 h at 316 °C under 1.4 MPa							
Flexural strength, GPa <sup>b</sup>	0.163	0.142	—	0.137	0.139	0.130	[45]
Flexural modulus, GPa <sup>b</sup>	133	124	—	127	130	126	
Interlaminar shear strength, MPa <sup>c</sup>	101	71	—	51.7	50.3	40.0	

<sup>a</sup>See Table 12 for fiber properties.<sup>b</sup>ASTM D790.<sup>c</sup>ASTM D2344.

commercially available [46], primarily for use in the electronics industry. However, it is relatively expensive. Research and development is in progress, with emphasis on lowering cost and improving the processability of these materials. Until a favorable combination of price, processability, and performance is achieved, quinoxaline polymers will remain materials of great potential but limited use.

The use of trade names or manufacturers does not constitute an official endorsement of such products or manufacturers, either expressed or implied, by the National Aeronautics and Space Administration.

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