

Polyphenylquinoxalines: Synthesis, Characterization, and Mechanical Properties*

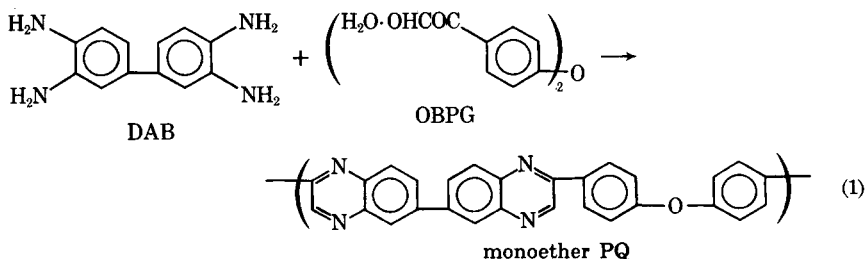
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Synopsis

The synthesis of polyphenylquinoxalines (PPQ) is discussed in detail. Solutions of PPQ at 20% solids content from stoichiometric quantities of pure reactants are generally metastable, increasing in viscosity and, in some cases, gelling. This can be alleviated without any appreciable detrimental effect upon the polymer by upsetting the stoichiometry of the reactants. Relatively high molecular weight polymer ($\eta_{inh} = 1.84$ dl/g; H₂SO₄, 0.5%, 25°C) can be obtained when the stoichiometry is upset by 2%. Several new PPQ are reported which contain multiple phenyl ether groups located in the para position of the substituted phenyl ring. Introduction of a phenoxy group decreased the T_g by 70°C. The properties of random and block copolymers of phenylquinoxaline and phenyl-*as*-triazine units are reported. Depending upon the processing conditions, PPQ Ti tensile shear specimens gave RT strength of 4900 psi and 316°C strength after 500 hr at 316°C of 1500 psi. Unidirectional high-modulus graphite composites provided RT flexural strength of 123,000 psi, flexural modulus of 15.6×10^6 psi, and interlaminar shear strength of 7000 psi.

INTRODUCTION

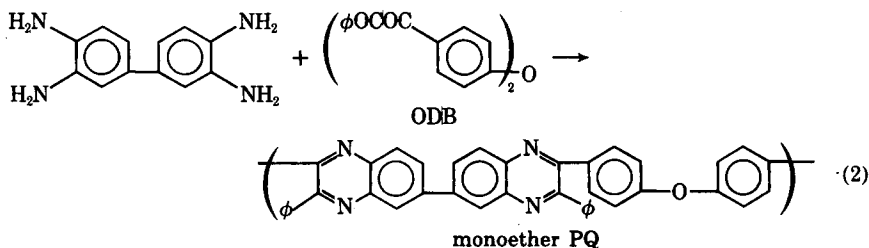
The synthetic route to polyquinoxalines (PQ) was initially proposed by Sorenson¹ in 1961 at a meeting of the American Chemical Society. At that time, Stille commented on the status of his work already underway on PQ which led to a series of papers²⁻⁴ and a patent.⁵ Concurrent with Stille's work, Sillion and co-workers were also investigating PQ through the same synthetic route which has been reported in papers^{6,7} and patents.⁸ This work involved the reaction of aromatic bis(*o*-diamines) such as 3,3'-diaminobenzidine (DAB) with aromatic bisglyoxals such as *p,p'*-oxybis(phenyleneglyoxal hydrate) (OBPG):



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In an attempt to improve the thermooxidative stability of PQ, polyphenylquinoxalines (PPQ) were prepared⁹ from the reaction of aromatic bis(*o*-diamines) such as DAB with aromatic bisbenzils such as *p,p'*-oxydibenzil (ODB):



The thermooxidative stability of the PPQ was shown to be significantly better than the PQ. In addition, the PPQ offers several other distinct advantages over the PQ such as easier synthesis of monomers and polymers, improved processability, and better solubility. As a result of their unique properties, a significant effort has concentrated on the synthesis¹⁰⁻¹² and the thermal characterization of PPQ.¹³⁻¹⁵ The potential of these polymers for use as functional and structural resins in a high-temperature environment has been demonstrated.^{16,17} The purpose of this paper is to report certain findings on PPQ which have not been previously reported.

DISCUSSION

Synthesis

The general procedure for phenylquinoxaline polymer synthesis involved the addition of the bis(1,2-dicarbonyl) reactant as a fine powder during ~3 min to a slurry of the tetraamine in 1:1 *m*-cresol/xylene at room tem-

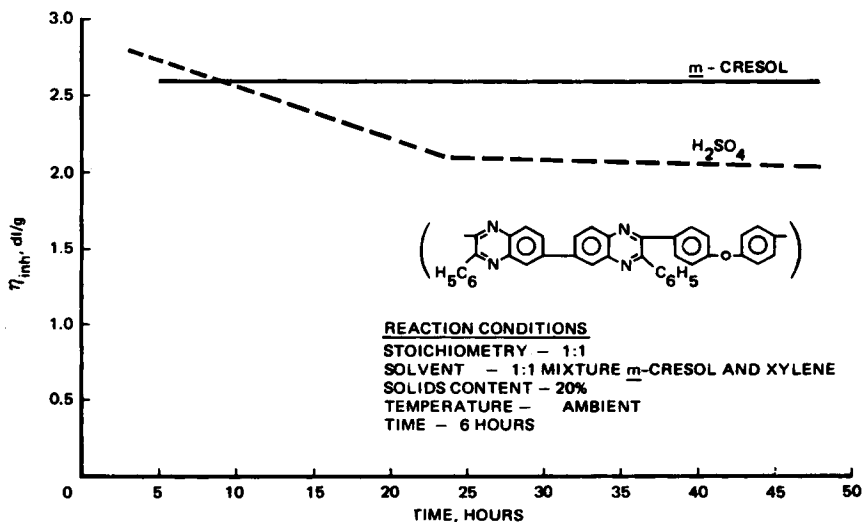
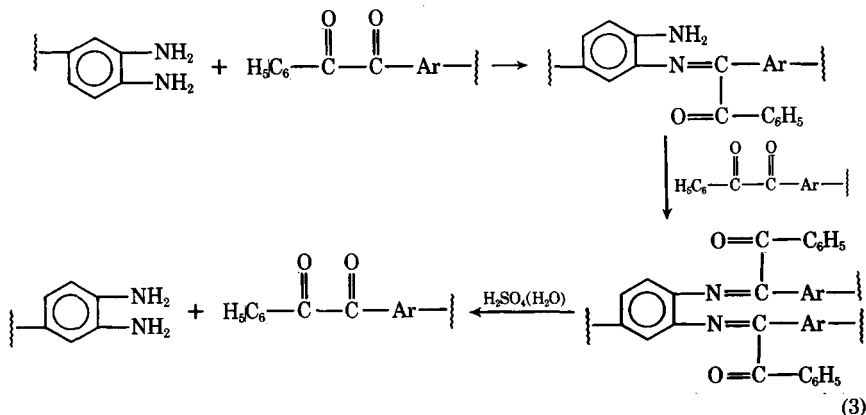


Fig. 1. Dilute solution viscosity of a PPQ (0.5% concentration at 25°C).

perature. When high-purity reactants are used in stoichiometric quantities at a solids content of 20% (w/v), the resulting PPQ solutions are metastable increasing in viscosity and in some cases gelling after stirring for several hours. The gel, once formed, is irreversible. The polymer can be isolated from the gelled state and generally redissolved at a lower solids content (e.g., 5% instead of 20%). This type of behavior was first observed in polyphenyl-*as*-triazines¹⁸ and is tentatively attributed to a combination of two factors, high molecular weight species and a small amount of branching. In some cases, evidence to support branching is based upon the fact that the dilute solution viscosity in concentrated sulfuric acid gradually decreases to a certain value and remains constant. The branched sites which are presumably Schiff bases are apparently cleaved by the acid:



The absence of carbonyl absorptions in the infrared spectrum of isolated polymer indicated that complete ring closure had occurred where possible, otherwise the incompletely ring-closed intermediate would also undergo cleavage, resulting in a decrease in the dilute solution viscosity. Viscosity behavior in concentrated sulfuric acid is given in Figure 1 for the monoether PPQ shown in eq. (2). The inherent viscosity (η_{inh} , 0.5% concentration at 25°C) of a fresh concentrated sulfuric acid solution was 2.8 dl/g and decreased to 2.1 after 24 hr. The η_{inh} in *m*-cresol (0.5% concentration at 25°C) remained unchanged at 2.6 dl/g after 48 hr. Only a small amount of branching is assumed to be present since the polymer is still soluble in *m*-cresol and other organic solvents (e.g., chloroform and *sym*-tetrachloroethane). In addition, certain properties such as the glass transition temperature (T_g) and the polymer softening temperature (PST) were essentially identical to that of another polymer sample of the same structure which failed to exhibit a decrease in the dilute solution viscosity [η_{inh} (0.5% H_2SO_4 solution at 25°C) = 2.6 dl/g]. A small degree of branching has also been proposed by Hagnauer and Mulligan¹⁹ to explain their findings on the dilute solution properties of a PPQ.

In some cases, polymer which had been isolated from a gelled solution (20% solids) exhibited no decrease in its dilute solution viscosity in concentrated sulfuric acid. Prior to gelling, a portion of the polymer solution

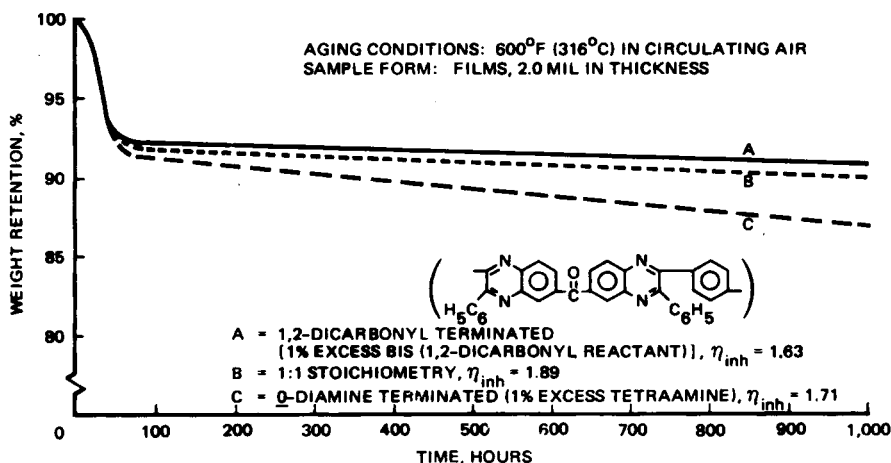


Fig. 2. Isothermal weight loss of PPQ.²⁰

was diluted to 10% solids. Since the 10% solution failed to gel, gelling in the more concentrated solution was tentatively attributed to high molecular weight forms and the associated factors. The polymers from the 10% and 20% solutions exhibited η_{inh} (0.5% *m*-cresol solution at 25°C) of 2.65 and 2.71 dl/g, respectively, and essentially identical T_g and *PST*. Early work⁹ had indicated a weight-average molecular weight for a PPQ with an η_{inh} of 2.16 of 247,000. More recent work¹⁹ has reported 350,000 weight-average and 34,000 number-average molecular weight for a PPQ with an intrinsic viscosity of 2.62.

The gelling phenomenon can be alleviated without any appreciable detrimental effect upon the polymer by upsetting the stoichiometry of the reactants.²⁰ The stoichiometry should be upset preferably in favor of the tetracarbonyl reactant, since PPQ with amino endgroups display lower thermooxidative stability as shown in Figure 2. Depending upon the solubility and reactivity of the reactants, the stoichiometry can be upset by as much as 2% and relatively high molecular weight polymer ($\eta_{inh} = 1.84$) can still be obtained. This was unexpected since in AA-BB condensation polymerizations, stoichiometric quantities of reactants are generally required to form high molecular weight polymers (excluding interfacial condensation). This polycondensation exhibits many features of an interfacial type polycondensation and, as explained by Morgan,²¹ the rate of polymerization is faster than the rate of mixing or dissolution such that there may be temporary interfaces within which polycondensation is proceeding independently of the stoichiometry of the two reactants in the complete system. The bis(1,2-dicarbonyl) compound is more soluble in the solvent mixture than the tetraamine. In some cases, when stoichiometric quantities of reactants were used, the solution viscosity increased significantly over a relatively short time without the formation of a com-

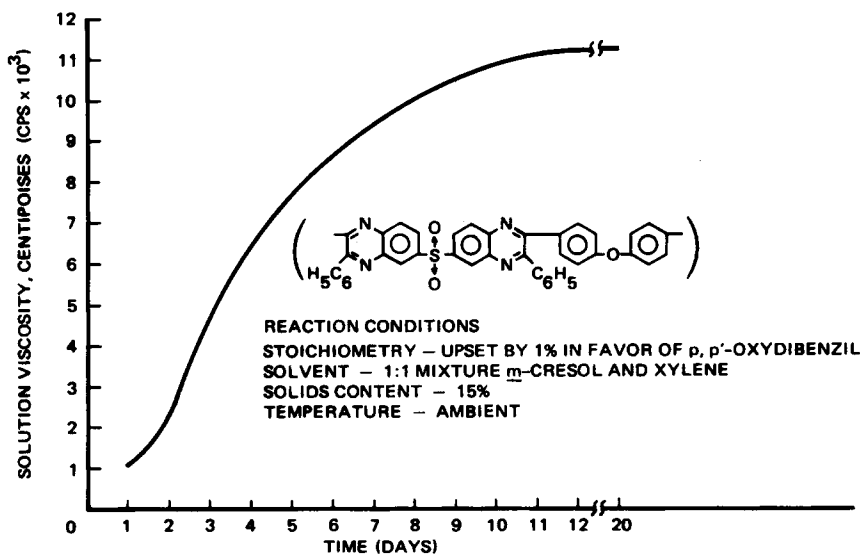


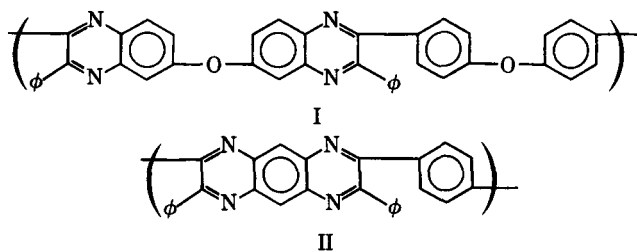
Fig. 3. Solution viscosity increase of a PPQ.

plete solution. For example, the reaction of stoichiometric quantities of DAB and *p*-bis(phenylglyoxylyl) benzene on a 0.1 mole scale at 20% solids in 1:1 *m*-cresol/xylene provided a viscous solution (Brookfield viscosity at 25°C = 50,000 cps) containing solid particles after stirring 0.5 hr. The solid particles were isolated and identified as unreacted DAB while the polymer shown to be of substantially high molecular weight ($\eta_{inh} = 2.4$, $\bar{M}_n = 39,000$). If the reaction was allowed to continue, gelation generally occurred in ~ 4 hr. Other less reactive tetraamines and bis(1,2-dicarbonyl) compounds required longer periods at room temperature to attain high molecular weight. For example, stoichiometry quantities of 3,3',4,4'-tetraaminodiphenylsulfone and ODB at 20% solids in 1:1 *m*-cresol/xylene required 22 hr to gel ($\eta_{inh} = 2.07$ dl/g). Gelling also occurred at 15% solids after 72 hr ($\eta_{inh} = 1.84$ dl/g), whereas no gelling occurred at 10% solids after 20 days ($\eta_{inh} = 1.61$ dl/g). When the stoichiometry was upset by 1% in favor of ODB, at 15% solids, the solution viscosity increased slowly over a period of 11 days as shown in Figure 3, and a polymer with an η_{inh} of 1.62 dl/g was obtained.

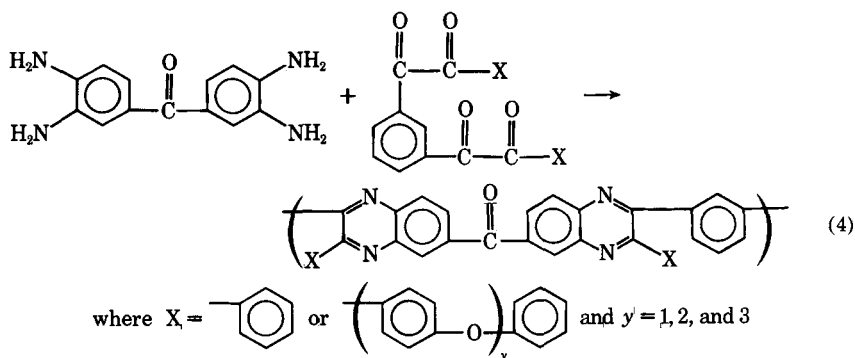
More than fifty different PPQ have been prepared and characterized from various combinations of seven different tetraamines and ten different bis-(1,2-dicarbonyl) compounds. At exact stoichiometry at 20% solids content, solutions of almost all of these PPQ gelled, whereas at 8% to 10% solids content, stable solutions of high molecular weight polymer were generally obtained. At 20% solids content, stable solutions of relatively high molecular weight PPQ can be readily prepared by upsetting the stoichiometry by 0.5% to 2.0% in favor of the bis(1,2-dicarbonyl) reactant.

Synthetic Control of Properties

The properties of the PPQ can be controlled to permit the tailoring of PPQ for specific applications. This has been done in past work by introducing certain moieties into the backbone of the polymer chain which impart rigidity or flexibility. In addition, the properties of certain PPQ have been controlled by the preparation of random and block type copolymers.²⁰ Wrasidlo¹⁴ has recently characterized twelve structurally different PPQ by calorimetric, dilatometric, dynamic mechanical, and dielectric techniques and showed that the T_g varied from a low of 258°C to a high of 395°C for polymers I and II, respectively:



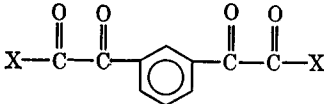

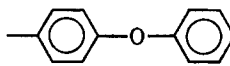
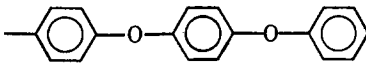
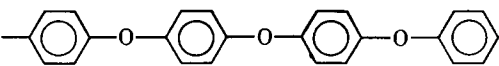
Recent work has shown that the T_g and other properties of PPQ can be significantly altered by placing flexibilizing pendent groups on the quinoxaline ring. Several new bis(1,2-dicarbonyl) reactants shown in Table I were reacted with 3,3',4,4'-tetraaminobenzophenone to yield the corresponding PPQ:



The T_g 's of the polymers varied from 200° to 285°C, with the largest decrease resulting from introduction of a phenoxy group in the para position of the substituted phenyl ring (see Table II).

The properties of the PPQ have also been significantly altered by introducing phenyl-*as*-triazine moieties within the backbone of the polymer. A series of phenylquinoxaline and phenyl-*as*-triazine copolymers of a random and block character were prepared. The random copolymers were prepared by adding *p*-bis(phenylglyoxylyl)benzene (*p*-BPGb) to a slurry of DAB and oxalamidrazone (OAD) according to the stoichiometry given in Table III. The random copolymers were prepared at 14% solids con-

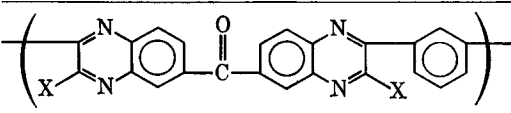

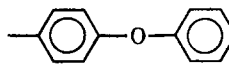
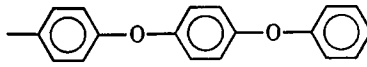
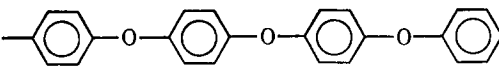
TABLE I
Characterization of Bis(1,2-dicarbonyl) Compounds

	X =	mp, °C	Elemental analysis ^a		
			C, %	H, %	O, %
		99–100 ^b	C ₂₂ H ₁₄ O ₄	—	—
		131.5– 132.5	C ₃₄ H ₂₂ O ₆	77.64 (77.55)	4.20 (4.21)
		170– 172	C ₄₆ H ₂₂ O ₆	77.97 (77.73)	4.29 (4.25)
		153– 154.5	C ₅₈ H ₃₈ O ₁₀	78.15 (77.84)	4.39 (4.28)

^a Theoretical values in parenthesis.

^b Lit. mp 98–99.5°C.¹¹

TABLE II
Characterization of Substituted Phenylquinoxaline Polymers

	X =	η_{inh} , dl/g ^a	T_g , °C ^a
		0.91	285
		0.72	215
		0.62	206
		0.61	200

^a 0.5% *m*-cresol solution at 25°C.

^b Determined by DSC, $\Delta T = 20^\circ\text{C}/\text{min}$, N₂.

tent in a 1:1 mixture of *m*-cresol and xylene by upsetting the stoichiometry by 1% in favor of the bis(1,2-dicarbonyl) reactant. The properties of the random copolymers having a distribution ratio of phenylquinoxaline to phenyl-*as*-triazine of 1:1 are given in Table III.

Block copolymer synthesis involved the preparation of low molecular weight forms of phenylquinoxaline and phenyl-*as*-triazine polymers. The stoichiometry for the phenylquinoxaline portion was adjusted to yield an oligomer rich in *o*-amino endgroups while the phenyl-*as*-triazine oligomer was rich in 1,2-dicarbonyl endgroups. The overall stoichiometry was up-

TABLE III
Characterization of Phenylquinoxaline and Phenyl-*as*-triazine Copolymers

Polymer	Molar amount of reactants ^a			η_{inh} , dl/g ^b	T_g , °C ^c	PDT, °C ^d
	DAB	OAD	<i>p</i> -BPGB			
PPQ	0.99	—	1.00	1.65	355	565
PPT	—	0.99	1.00	1.45	302	394
RaCo (1:1)	0.495	0.495	1.00	1.03	319	391
RlCo (1:1)	0.495	0.495	1.00	1.51	321	392
Blend (1:1)	1:1 molar blend of PPQ and PPT			1.47	303 and 355	393

^a Stoichiometry upset by 1% to avoid gelling.

^b 0.5% *m*-cresol solution at 25°C.

^c Determined by DSC at $\Delta T = 20^\circ\text{C}/\text{min}$, N_2 .

^d Polymer decomposition temperature, initial break, determined by TGA at $\Delta T = 6^\circ\text{C}/\text{min}$, N_2 (see Fig. 4.).

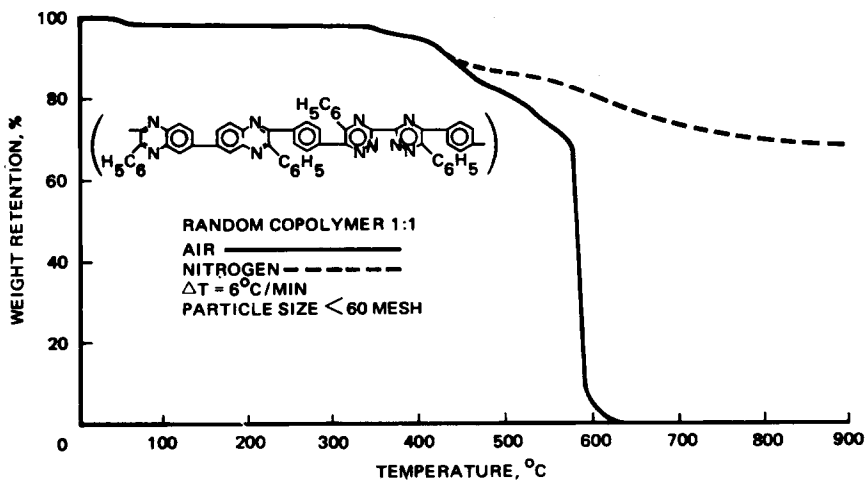


Fig. 4. Thermogravimetric analysis of a 1:1 phenylquinoxaline:phenyl-*as*-triazine random copolymer.

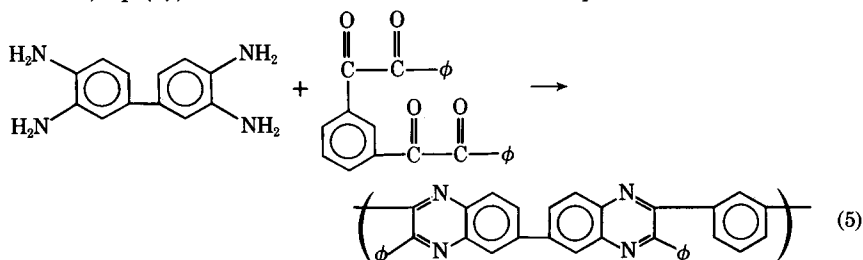
set by 1% in favor of *p*-BPGB. The oligomeric solutions were combined and further reacted to provide a block copolymer having a distribution ratio of phenylquinoxaline to phenyl-*as*-triazine of 1:1. The properties of the block copolymer as well as a 1:1 molar blend of the homopolymers are given in Table III.

In general, incorporating phenyl-*as*-triazine moieties within the backbone of PPQ does not appear to offer any advantageous effect. The thermal stability and thermooxidative stability is significantly lowered while the processability is not greatly altered. Phenyl-*as*-triazine polymers exhibit long term stability at 500°F (260°C) in air, whereas PPQ exhibit good retention of properties after long term (e.g., 1000 hr) at 600°F (316°C).

Mechanical Properties

The processability of PPQ is exceptional when compared to other all aromatic heterocyclic polymers. The PPQ are prepared in soluble high molecular weight form which exhibit excellent processability relative to other high-temperature polymers with the evolution of little or no volatiles. Solutions of PPQ can be conveniently used to prepare prepreg or adhesive tape. Depending upon the structure of the polymer, the total volatile content of the tape or prepreg can be reduced to 0.1% while still retaining processability. The processability is attributed to the thermoplastic nature of the polymer.

The polymer from the reaction of DAB with *m*-bis(phenylglyoxalyl)-benzene, eq. (5), was evaluated in adhesive and composite work:



The polymer was prepared in 1:1 *m*-cresol/xylene at 20% solids at ambient temperature by upsetting the stoichiometry by 0.5% in favor of the bis-(1,2-dicarbonyl) reaction. The polymer solution exhibited a viscosity of 5200 cps (25°C), and the polymer exhibited an η_{inh} (0.5% *m*-cresol solution at 25°C) of 0.98 dl/g and a T_g (by DSC at 20°C/min in nitrogen) of 318°C.

In adhesive work, an unformulated tape (112 E-glass A1100 finish, 11 mils thick, 0.2% volatiles) of the *m*-phenylene PPQ was used to fabricate tensile shear specimens using titanium (6A1-4V) adherend having a phosphate fluoride surface treatment. Curing was accomplished at 50 psi in a press starting at room temperature and increasing the temperature to that designated in Table IV.

TABLE IV
Preliminary PPQ Tensile Shear Strength on Ti(6-4)

Test condition ^a	Tensile shear strength, psi	
	Cure 600°F, 1 hr	Cure 1 hr each at 750, 800 and 850°F
Room temperature	4900	3500
450°F after 10 min at 450°F	3700	—
450°F after 8000 hr at 450°F	3600	—
600°F after 10 min at 600°F	700 ^b	2000
600°F after 500 hr at 600°F	—	1500

^a Aged in circulating air (115 ml/min).

^b Thermoplastic failure.

TABLE V
Preliminary Unidirectional Flat Laminate Properties (Hercules HM-S)

Test conditions	Flexural strength, psi	Modulus, psi $\times 10^6$	Interlaminar* shear strength, psi
RT	123,000	15.6	7000
600°F after 10 min	71,000	11.1	5200
600°F after 200 hr at 600°F	56,000	10.3	4500
600°F after 500 hr at 600°F	48,000	9.7	4200

* Short beam (span to depth ratio 4:1).

Unidirectional laminates were fabricated at 750°F (1 hr) and at 800°F (2 hr) under 200 psi from prepreg prepared by solution coating a high-modulus graphite fiber (Hercules HM-S) which was dried to a total volatile content of 0.21%. The 4" \times 5" \times 11 ply PPQ laminates provided the properties reported in Table V.

EXPERIMENTAL

Reactants

3,3'-Diaminobenzidine. This tetraamine was obtained commercially and recrystallized from water (100 g/5 l.) containing a pinch of sodium dithionite under nitrogen. Near-white crystals, mp 176.5–177.5°C (lit.²² mp 179–180°C) were obtained in 70% recovery.

3,3',4,4'-Tetraaminodiphenyl Sulfone. The pink tetraamine as received was recrystallized from water (122 g/4 l.) containing a pinch of sodium dithionite under nitrogen. White crystals were obtained in 80% recovery which melted at 179–180°C (lit.²³ mp 173–174°C).

3,3',4,4'-Tetraaminobenzophenone. This tetraamine was obtained from a commercial source and recrystallized from a 1:2 mixture of N,N-dimethylformamide and water (100 g/3.5 l.) under nitrogen. Yellow needles, mp 216–217.5°C (lit.²⁴ mp 217°C), separated in 78% recovery.

Oxalamidrazone. Following a known procedure,¹⁸ cyanogen was bubbled through a cold solution of anhydrous alcohol containing hydrazine (97%) to yield oxalamidrazone as a white crystalline material, mp 178–179°C (dec, introduced into preheated oil bath at 170°C) (lit.¹⁸ mp 179–180°C dec).

Bis(1,2-dicarbonyl) Compounds. *p,p'*-Oxydibenzil was prepared following a known procedure²⁵ and obtained as yellow crystals, mp 106–107°C (lit.²⁶ mp 106.4–107.4°C). *p*-Bis(phenylglyoxylyl)benzene was prepared according to a known procedure¹¹ and obtained as yellow crystals, mp 125–126 (lit.²⁷ mp 125–126°C). The various bis(1,2-dicarbonyl) compounds reported in Table I were prepared by the following representative procedure. A solution of the diacid chloride of *m*-phenylenediacetic acid (92 g, 0.4 mole) and diphenyl ether (340 g, 210 mole) in carbon disulfide

(400 ml) was added dropwise during 3 hr to a stirred slurry of anhydrous aluminum chloride (133 g, 1.0 mole) in carbon disulfide (600 ml) at 5° to 10°C. After complete addition, the reaction mixture was stirred at ambient temperature for 18 hr followed by pouring onto ice and hydrochloric acid. Methylene chloride (400 ml) was added to facilitate separation. The organic phase was washed twice with water and concentrated to dryness. The residual white solid was washed thoroughly with *n*-hexane in a Waring blender. The resulting hexane-insoluble white solid (182 g, 95% yield) melted at 120–122°C. The intermediate diketone (182 g, 0.38 mole) and selenium dioxide (84.4 g, 0.76 mole) were refluxed in glacial acetic acid (2 liters) for 6 hr. A hot filtration followed by cooling provided yellow crystals (171 g), mp 130.5–132.5°C, which were recrystallized from a 1:1 mixture of benzene and alcohol (1.2 liters). The resulting yellow crystals (139 g, 70% yield from oxidation step) of *m*-bis(*p*'-phenoxyphenylglyoxalyl)benzene melted at 131.5–132.5°C. Further characterization is given in Table I.

Polymers

The homopolymers were prepared according to the following representative procedure:

m-Bis(*p*'-phenoxyphenylglyoxylyl)benzene (5.263 g, 0.010 mole) as a powder was added rapidly to a stirred slurry of 3,3',4,4'-tetraaminobenzophenone (2.411 g, 0.00995 mole) in a 1:1 mixture (31 ml) of *m*-cresol and xylene. The reaction mixture was stirred at ambient temperature for 18 hr to provide a viscous orange solution. A portion of the solution was slowly poured into methanol in a Waring blender to precipitate a fibrous yellow solid which was boiled twice in methanol and dried at 130°C in vacuo for 4 hr. Characterization of the polymer is given in Table II.

The random copolymer reported in Table III was prepared in the following manner. *p*-Bis(phenylglyoxylyl)benzene (3.424 g, 0.010 mole) as a powder was added to a stirred slurry of oxalamidrazone (0.5747 g, 0.00495 mole) and 3,3'-diaminobenzidine (1.061 g, 0.00495 mole) in a 1:1 mixture (20.2 ml) of *m*-cresol and xylene. The reaction mixture was stirred at ambient temperature for 18 hr to provide a viscous orange solution. The polymer was isolated as previously described for the homopolymers and characterized as shown in Table III.

The block copolymer reported in Table III was prepared in the following manner. *p*-Bis(phenylglyoxylyl)benzene (2.054 g, 0.006 mole) was added to a stirred slurry of oxalamidrazone (0.5747 g, 0.00495 mole) in a 1:1 mixture (10 ml) of *m*-cresol and xylene. The resulting reaction mixture was stirred for 18 hr at ambient temperature to provide a yellowish orange solution of phenyl-*as*-triazine oligomer end-capped with bis(1,2-dicarbonyl) groups. In another flask, *p*-bis(phenylglyoxylyl)benzene (1.370 g, 0.004 mole) as a powder was added to a stirred slurry of 3,3'-diaminobenzidine (1.061 g, 0.00495 mole) in a 1:1 mixture of *m*-cresol and xylene.

The reaction mixture was stirred for 18 hr at ambient temperature to afford a red solution of phenylquinoxaline oligomer end-capped with *o*-diamine groups.

The phenylquinoxaline oligomeric solution was added to the stirred phenyl-*as*-triazine solution using additional solvent (5 ml) to rinse the flask. The solution was stirred for 18 hr at ambient temperature to yield a viscous orange solution. The major increase in solution viscosity occurred upon stirring the first hour. The block copolymer was isolated as previously described for the homopolymers and characterized as shown in Table III.

Thermal Analysis

Thermogravimetric analysis was performed using the du Pont 950 thermogravimetric analyzer at a heating rate of 6°C/min in air and in nitrogen. Glass transition temperatures were determined using the du Pont differential scanning calorimetry cell at a heating rate of 20°C/min in nitrogen. The T_g was taken at the inflection point of the ΔT -versus-temperature curve.

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