

# Polyphenylquinoxalines Containing Pendant Phenylethynyl Groups: Preliminary Mechanical Properties

PAUL M. HERGENROTHER, *NASA Langley Research Center, Hampton, Virginia 23665*

## Synopsis

Polyphenylquinoxalines (PPQ's) containing various amounts of crosslinkable pendant phenylethynyl groups were prepared from the reaction of 3,3',4,4'-tetraaminodiphenyl ether, 4,4'-oxydibenzil, and 4,4'-oxybis(4"-phenylethynylbenzil). The distribution of the pendant phenylethynyl groups along the polymer chain was varied in an attempt to alter the properties of the polymers. Preliminary film, adhesive, and laminate properties of PPQ void of pendant crosslinkable groups and containing pendant phenylethynyl groups were determined. The thermally induced reaction of the phenylethynyl group crosslinked the polymer which resulted in better dimensional stability at elevated temperatures.

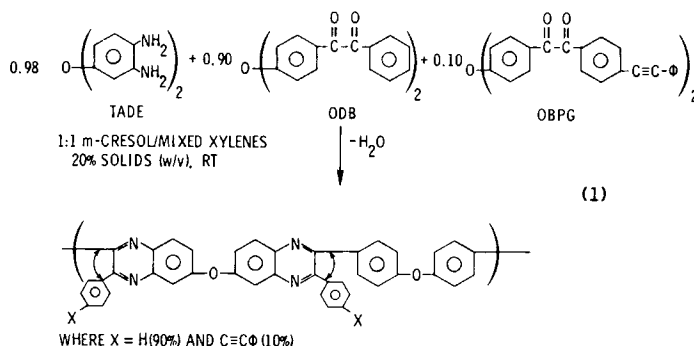
## INTRODUCTION

Polyphenylquinoxalines (PPQ's) are high temperature thermoplastics which have displayed respectable properties as adhesives,<sup>1-5</sup> composite matrices,<sup>2,5-7</sup> and films.<sup>8</sup> Typical of thermoplastics, PPQ's under load undergo deformation at temperatures near their glass transition temperatures. Several routes have been investigated to improve their high temperature dimensional stability (see references in Ref. 9). An attractive method involved placing pendant phenylethynyl groups along the polymer chain. These groups undergo reaction at high temperatures to provide crosslinking. The primary objective of the work reported herein was to determine what effect the pendant phenylethynyl groups have upon the physical and mechanical properties of cured and uncured PPQ's.

## EXPERIMENTAL

**4,4'-Oxybis(4"-Phenylethynylbenzil)(OBPB):** This compound was prepared following a known procedure.<sup>9</sup> The crude product from the reaction of 4,4'-oxybis(4"-bromobenzil) and phenylacetylene using a palladium catalyst was isolated in 94% yield as a pale yellow solid, mp 174–176°C. Recrystallization from acetone (25 g/L) using charcoal afforded 4,4'-oxybis(4"-phenylethynylbenzil) in 77% recovery as a yellow crystalline solid, mp 181–182°C (lit<sup>9</sup> mp 181–182.5°C).

**Other Monomers and Solvents:** 4,4'-Oxydibenzil (ODB), mp 106–107°C (lit<sup>10</sup> mp 106.4–107.4°C), was prepared according to a known procedure.<sup>11</sup> 3,3',4,4'-Tetraaminodiphenyl ether (TADE) was obtained commercially and recrystallized from water (50 g/L) using a pinch of sodium dithionite under ni-



Scheme I. Eq. 1.

trogen to afford light tan needles, mp 152–153°C (lit<sup>12</sup> mp 149.5–151°C), in 81% recovery. Commercial grade *m*-cresol (97% purity) and mixed xylenes were used as received.

**Polymer:** Polymer synthesis (Scheme I) was conducted on a 0.02–0.20-mol scale in a 1:1 mixture of *m*-cresol and mixed xylenes at a concentration (w/v, based upon monomers) of 20% by upsetting the stoichiometry by 2–4 mol % on a 0.02–0.2-mol scale, respectively, in favor of the bis( $\alpha$ -diketone). The standard PPQ was prepared by adding TADE as a fine powder to a stirred solution of ODB. After an exotherm to 42°C on a 0.2-mol scale, the reaction mixture was stirred overnight at ambient temperature to yield a viscous amber solution.

Three different methods were employed to synthesize the phenylethynyl containing PPQ using 10 mol % of OBPG on a 0.05-mol scale. Method 1 was the same as used to prepare the standard PPQ and simply involved the addition of TADE (11.170 g, 0.0485 mol) as a fine powder to a stirred solution of ODB (19.548 g, 0.045 mol) and OBPG (3.173 g, 0.005 mol) in the solvent mixture (135 mL). In method 2, TADE as a fine powder was added to a stirred solution of ODB and stirred at ambient temperature for 6 h. OBPG was then added, and the reaction mixture stirred at ambient temperature overnight. Method 3 involved the preparation of oligomers and subsequent reaction of the oligomers with each other as indicated. TADE (9.212 g, 0.040 mol) as a fine powder was added to a stirred solution of ODB (19.548 g, 0.045 mol) in the solvent mixture (80 mL) and the reaction mixture was stirred for 6 h at ambient temperature to form a yellowish orange solution. In another flask, TADE (1.958 g, 0.0085 mol) as a fine powder was added to a stirred solution of OBPG (3.173 g, 0.005 mol) in the solvent mixture (30 mL) and the reaction mixture was stirred for 6 h at ambient temperature to form a reddish orange solution. The latter oligomeric solution was added to the former solution using the solvent mixture (25 mL) as wash to effect good transfer. The resultant reaction was stirred at ambient temperature overnight to yield a viscous amber solution.

Polymers for adhesive and composite evaluation as well as other PPQ's containing various amounts of pendant phenylethynyl groups were prepared by method 1. Polymer was isolated from a portion of each solution by quenching in methanol in a blender. The resultant fibrous yellow solid was thoroughly washed in boiling methanol and dried at 90°C in air. Inherent viscosities were determined on 0.5% solution of polymer in *m*-cresol at 25°C.

**Films:** The polymer solution as-prepared was centrifuged, doctored onto plate glass, and subsequently dried at 45–50°C to a tack-free form in a dust-proof chamber. Further stage-drying was performed to a final temperature of 200°C *in vacuo* overnight. The films were further conditioned by heating in air from 200°C to 325°C during 6 h and maintaining at 325°C for 1 h. Testing was performed according to ASTM-D882.

**Adhesive Specimens:** Standard tensile shear specimens (bond area, 1.0 in. wide  $\times$  0.5 in. overlap) were fabricated from four-fingered titanium (6A1-4V) panels having a Pasa-Jell 107 (source: Semco Div., Products Research and Chemical Corp.; consists primarily of sodium dichromate, hydrofluorosilicic, and nitric acids) surface treatment. The treated surface was primed within a few hours with a 5% PPQ solution. The primed coat was stage-dried in air to a final temperature of 250°C. An unformulated tape was prepared by brush coating the PPQ solution onto 112 E-glass fabric (A-1100 finish) secured on a frame. The initial coat was a 5% solution followed by three to four coats with the as-prepared PPQ solution until a dried tape thickness of  $\sim$ 12 mils was obtained. Each coat was dried in a forced air oven for 1 hr each at  $\sim$ 100,  $\sim$ 150, and  $\sim$ 200°C. After drying the final coat, the tape was dried overnight at  $\sim$ 180°C *in vacuo* to reduce the volatile content to  $<2\%$ . Tensile shear specimens were fabricated by introducing a jig containing the assembly into a press at RT, applying 200 psi, heating to 316°C under 200 psi during 45 min, and maintaining under these conditions for 0.5–2.0 h. In some instances, a post-cure was performed at 371°C for 2 h in the press. Testing was conducted according to ASTM D1002.

**Laminates:** Prepreg was prepared by brush coating drum-wound high tensile strength graphite/carbon fiber (Celanese Celion-6000) with a solution of PPQ. Initially, a dilute solution (5% solids, w/v) was applied to the fiber on the revolving drum and dried while rotating under heat lamps for 16 h (temperature of 110°C). The as-prepared PPQ solution (20% solids) was similarly applied and initially dried. The prepreg was further dried by placing 12 in.  $\times$  7 in. pieces sandwiched between 181 Style E-glass and glass plates under a weight to retain flatness into a heated oven. The prepreg was dried at 200°C *in vacuo* for 16 h to reduce the volatile content to  $<2\%$ . Unidirectional laminates (3 in.  $\times$  7 in.  $\times$  8 ply or 12 ply) were fabricated in a stainless steel mold using a ply of teflon fabric (TX 1040) and 2 plies of 181 Style E-Glass on each side of the layup. The laminates were fabricated by introducing the mold containing the layup into the press at RT, applying 200 psi, heating to 371°C during 1 h under 200 psi, and maintaining under these conditions for 1 h. Select specimens were post-cured unrestrained at 371°C for 4 h. Flexural strength tests were conducted according to ASTM D-790-66. Short beam shear specimens were tested at a span-to-depth ratio of 4:1.

**Thermal Characterization:** Differential scanning calorimetric (DSC) curves were obtained with a DuPont Model 990 thermal analyzer in combination with a standard DuPont DSC cell. Samples were hermetically sealed in DuPont supplied aluminum cups and subsequently run in air or nitrogen atmosphere at a heating rate of 20°C/min. The apparent glass transition temperature ( $T_g$ ) was taken at the inflection point of the  $\Delta T$  vs. temperature curve. Torsional braid analyses (TBA) were performed at a heating rate of 3°C/min in a nitrogen atmosphere over the temperature range of  $-100^\circ\text{C}$  to  $+325^\circ\text{C}$ . Heatup and

cooldown curves were obtained on the same sample. Thermal mechanical analyses (TMA) were obtained on films and moldings at a heating rate of 5°C/min. Isothermal aging was performed on polymer films and individual adhesive and laminate test specimens in circulating air in a Blue M Oven Model No. POM-5580 EX.

## RESULTS AND DISCUSSION

**Synthesis:** A standard PPQ was prepared from the reaction of TADE and ODB in a 1:1 mixture of *m*-cresol and mixed xylenes at ambient temperature. As with the synthesis of most PPQ's from high purity monomers, the stoichiometry was upset in favor of the bis( $\alpha$ -diketone) to avoid an extremely viscous solution or gelation.<sup>7</sup> Using the same basic PPQ, different amounts of pendant phenylethynyl groups were introduced within the polymer by substituting OBPB for ODB. As indicated in Table I, PPQ's containing 2, 5, 10, and 30 mol % of pendant phenylethynyl groups were prepared. To alter the distribution of pendant phenylethynyl groups in the polymer, three different synthetic methods were investigated employing 10 mol % of OBPB. In method 1, TADE was added to a stirred solution of OBPB and ODB to provide a polymer with random distribution of the pendant phenylethynyl groups. In method 2, TADE was reacted with ODB for several hours and OBPB was subsequently added and was reacted to provide more of a block-type distribution of pendant groups. In method 3, *o*-diamine-terminated oligomer was prepared from the reaction of excess TADE with OBPB. The oligomeric solution was added to a stirred solution of benzil-terminated oligomer which was prepared from the reaction of TADE with excess ODB. In this manner, block-type distribution of pendant phenylethynyl groups were introduced into the polymer. Overall, the same stoichiometry was maintained in methods 1, 2, and 3. Gel permeation (size exclusion) chromatograms of the polymers prepared by the three methods are shown in Figure 1. The GPC

TABLE I  
Characterization of Polymers [Eq. (1)]

X [see eq. (1)]	Syn. method (see Exptl)	Scale (mol)	$\eta_{inh}^a$ (dL/g)	DSC data (°C) <sup>b</sup>		TBA data (°C) <sup>c</sup>	
				Initial $T_g$	Final $T_g$	Heatup peaks	Cooldown peaks
H	1	0.02	0.65	255	256	-38,252	256
	1	0.20	0.55	253	255	-36,251	254
C≡CØ	1	0.02	0.78	254	258	-30,251	257
H (98%)							
C≡CØ	1	0.02	0.72	252	263	-35,248	260
H (95%)		0.20	0.67	252	262	-32,250	262
C≡CØ	1	0.05	0.76	254	281	-36,252	268
H (90%)	2	0.05	0.72	254	281	-32,251	269
	3	0.05	0.71	253	282	-31,253	269
C≡CØ	1	0.02	0.73	252	ND <sup>d</sup>	-34,253	274
H (70%)							

<sup>a</sup> Inherent viscosity, 0.5% solution in *m*-cresol at 25°C.

<sup>b</sup> Heating rate 20°C/min, heated to 400°C, static air, quenched, and rerun.

<sup>c</sup> Heating rate 3°C/min, heated to 325°C, nitrogen atmosphere.

<sup>d</sup> Not detected.

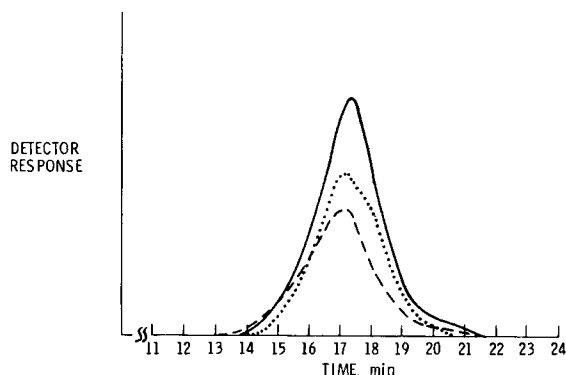


Fig. 1. Gel permeation (size exclusion) chromatograms; PPQ containing 10 mol %, pendant  $\text{—C}\equiv\text{C}\text{O}$  prepared by different methods: (—) method 1: all monomers mixed together; (---) method 2: TADE reacted with ODB, then OBPB added; (.....) method 3: oligomer from TADE and ODB reacted with oligomer from TADE and OBPB. Solvent: chloroform; column:  $10^6$ ,  $10^5$ ,  $10^4$ ,  $10^3$   $\mu$ -Styragel; flow: 2.0 mL/min [11.7 MPa (1700 psi)]; detector: UV (254 nm); concentration:  $\sim 5$   $\mu\text{g}/\mu\text{L}$ ; sample size:  $\sim 3$ –4  $\mu\text{g}/\mu\text{L}$ .

curves of the polymers prepared by methods 1 and 2 are very similar, displaying about the same molecular weight distribution and peak retention time. The GPC curve of the polymer prepared by method 3 has a shoulder and a slightly more narrow molecular weight distribution. Although premature, the various characterization tests to be discussed failed to display any discernable difference due to the distribution of pendant phenylethynyl groups along the polymer chain. The properties of the PPQ's with and without phenylethynyl groups may be too similar such that the characterization tests employed were not discriminating enough to detect any difference.

Characterization of the polymers is presented in Table I. The molecular weight as indicated by inherent viscosities in the 0.55–0.76 dL/g range was intentionally controlled in the intermediate range by upsetting the stoichiometry in favor of the bis( $\alpha$ -diketone). In this manner, stable solutions at concentrations of 20% (w/v, based upon weight of monomers) were prepared. If stoichiometric quantities of monomers were used at 20% solids, gelation generally occurred within 6–8 h. At 15% concentration, stoichiometric quantities of monomers provided extremely viscous solutions of polymers having inherent viscosities as high as 2.4 dL/g.

**Solubility Characteristics:** The uncrosslinked PPQ containing various amounts of phenylethynyl groups as well as the standard PPQ are readily soluble at RT at concentrations (w/v) as high as 30% in *m*-cresol (very viscous solutions), 1:1 mixtures of *m*-cresol with xylene or toluene, chloroform (moderately viscous solutions), and *sym*-tetrachlorethane. Transparent yellow films dried in air for 1 h at 225°C were readily soluble in chloroform. However, transparent orange films from the standard PPQ as well as from the PPQ containing various amounts of phenylethynyl groups which were dried for 1 h at 325°C in air were insoluble in chloroform or *m*-cresol. Swelling was observed in chloroform (24-h immersion) for the 325°C cured films from the standard PPQ and the PPQ containing 2, 5, and 10 mol % phenylethynyl groups whereas swelling was not observed in *m*-cresol. The degree of swelling decreased as the mol % of phenylethynyl groups

increased. The 325°C cured film from the PPQ containing 30 mol % phenylethynyl groups exhibited only very slight swelling in chloroform. Slight crosslinking occurred in the 325°C dried standard PPQ film probably through oxidative coupling of aromatic rings and/or through the terminal benzilyl groups. This is evidenced by an increase in the  $T_g$  (255–261°C) and swelling in chloroform.

**Thermal Characterization:** The  $T_g$  of the standard PPQ (void of phenylethynyl groups) was 254–256°C as determined by DSC or TBA at different heating rates. Representative DSC curves are shown in Figure 2. The broad endotherm peaking at 75°C is attributed to adsorbed moisture (sample run on a humid day). The sample exhibited a  $T_g$  at 252°C followed by a very strong exotherm starting at 280°C due to the reaction of the phenylethynyl groups. The sample was heated to 400°C, removed from the DSC cell, quenched, and rerun. The second run displayed a more intense transition attributed to the  $T_g$  at 263°C, again followed by an exotherm. The  $T_g$ 's by DSC reported in Table I were determined in the above manner. The introduction of various amounts (2, 5, 10, and 30 mol %) of pendant phenylethynyl groups in place of the para hydrogen on the pendant phenyl group had little effect upon the  $T_g$ . This was contrary to previous work with a different PPQ backbone where the presence of the pendant phenylethynyl groups caused an increase in the  $T_g$ .<sup>9</sup> As the amount of phenylethynyl groups increased, the  $T_g$ 's of the 400°C exposed polymers also increased due to higher crosslink density. In the representative TBA curves in Figure 3, the low temperature (–34°C) relaxation was originally thought to be due to motion of the pendent phenyl and phenylethynyl groups.<sup>9</sup> However, a linear polyquinoxaline ( $\eta_{inh} = 0.57$  dL/g and  $T_g = 261^\circ\text{C}$ ) prepared from the reaction of TADE and 4,4'-oxybis(phenylglyoxal hydrate) in *m*-cresol also exhibited a relaxation at –60°C. This suggests that the low temperature relaxation may be due to motion of an in-chain portion of the molecule. A damping peak occurred at 253°C (Fig. 3), which coincided with a rapid change in rigidity. After heating to 325°C, the cooldown curve displayed a higher damping peak at 274°C due to crosslinking. As shown in Table I, the initial  $T_g$ 's by TBA were essentially the same for all the polymers. As the amount of phenylethynyl groups increased, the cooldown damping peak temperature ( $T_g$ ) increased due to higher crosslink density.

In Figures 4 and 5, DSC curves are shown of a PPQ containing 30 mol % of phenylethynyl groups which had been conditioned at various temperatures in nitrogen and air, respectively. In each environment, a single sample was heated to the temperatures underlined on the figure, held for 15 min, removed from the cell, quenched, and rerun. These steps were then repeated at higher temperatures with the same sample. As shown in Figure 4, as the sample was exposed to higher temperatures in nitrogen, the transition attributed to the  $T_g$  became more diffuse and occurred at higher temperatures. After heating for 15 min at 375°C (run 5) in addition to 15 min each at 275°C, 300°C, 325°C, and 350°C, the  $T_g$  was 282°C, an increase of 30°C above the initial  $T_g$ . In Figure 5, the first three runs in air gave essentially the same results as observed in nitrogen. However, pronounced differences are evident in run 4 which displayed a mild transition at 273°C attributed to the  $T_g$ , followed by a weak exothermic peak at 304°C. Run 5 in static air showed no  $T_g$  but a strong exotherm peaking at 320°C. The next run exhibited an extremely strong exotherm peaking at 351°C

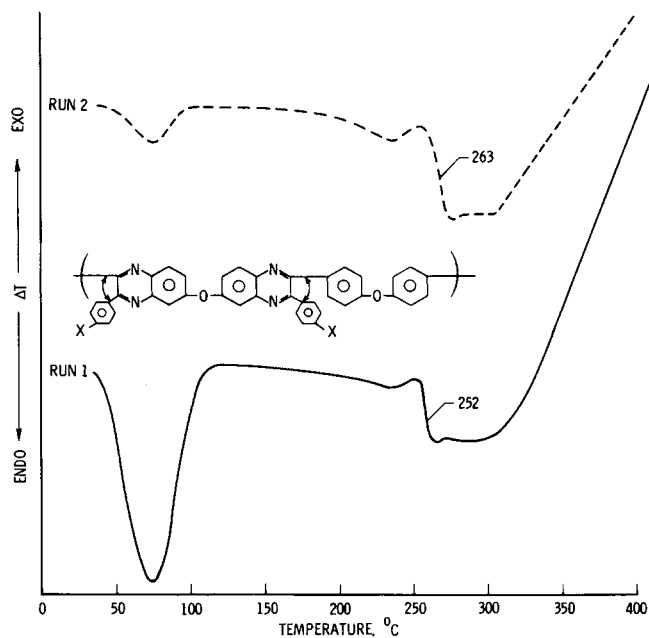


Fig. 2. Differential scanning calorimetric curves. Heating rate: 20°C/min; atmosphere: static air; sample size: 7.4 mg; sensitivity: 0.2 mcal/s-in. X = H (95%) and C≡CØ (5%).

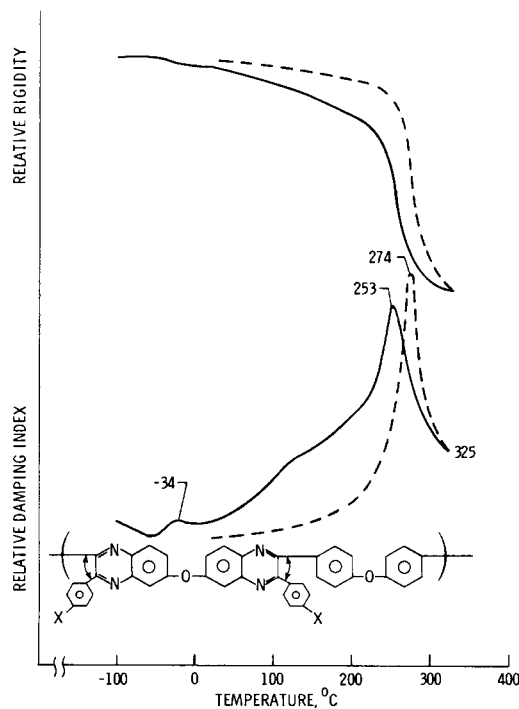


Fig. 3. Torsional braid analysis curves. Heating rate: 3°C/min; atmosphere: nitrogen; heatup (—); cooldown (---). X = H (70%) and C≡CØ (30%).

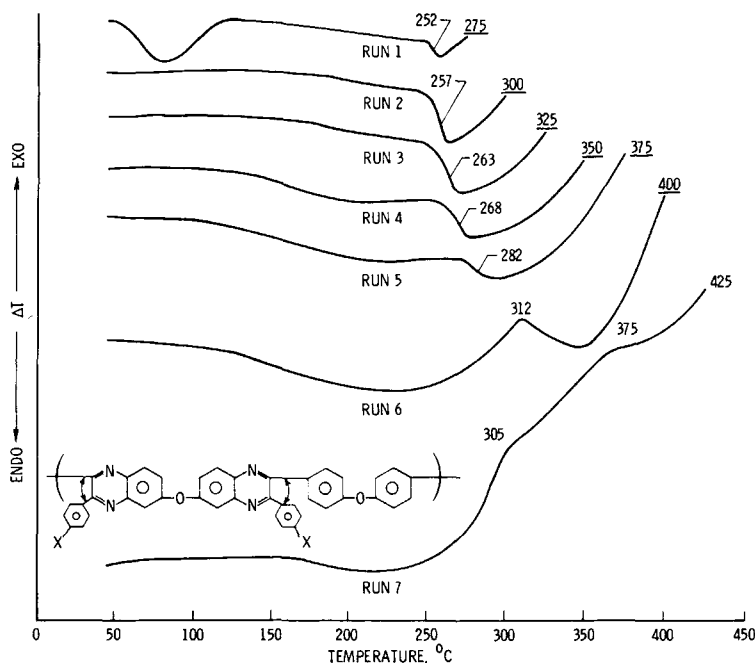


Fig. 4. Differential scanning calorimetric curves. Heating rate: 20°C/min; atmosphere: nitrogen; sample weight: 7.5 mg; sensitivity: 0.1 mcal/s-in. X = H (70%) and C≡C (30%).

(the pen had gone off scale and was attenuated to record the peak exotherm). These exotherms are presumably due to the curing reaction of the phenylethynyl groups although the nature of the product is unknown. Other samples of the same polymer ( $T_g = 252^\circ\text{C}$ ) in powder form were individually exposed to  $325^\circ\text{C}$  in flowing air and in nitrogen for 0.5 h. The  $T_g$  as determined by DSC increased to  $281^\circ\text{C}$  for the air-exposed sample and to  $273^\circ\text{C}$  for the nitrogen-exposed sample. Both samples were a more intense yellow color than the original sample. It appears the crosslinking reaction is accelerated in air although it is not known if the reaction mechanism is the same in both air and nitrogen. Samples cured in air and in nitrogen did not exhibit any significant difference in their infrared spectra. By DSC and TBA, no differences were detected as a function of synthetic method (distribution of pendant crosslinking groups) for the PPQ containing 10 mol % of phenylethynyl groups.

Polymer fusion temperatures were determined by placing powder samples sandwiched between aluminum foil into a press preheated to various temperatures, applying 200 psi, holding for 5 min and observing the ability to form transparent films. The PPQ void of phenylethynyl groups form a tough transparent lemon yellow film at  $301^\circ\text{C}$ . The PPQ containing 5, 10, and 30 mol % pendant phenylethynyl groups formed transparent films at 316, 325, and  $357^\circ\text{C}$ . Since the molecular weight of the polymers are about the same as suggested by inherent viscosities, the difference in flow characteristic is attributed to the phenylethynyl group. No difference in flow characteristic as a function of the distribution of the pendant phenylethynyl groups could be detected. In conducting comparative processing studies of this type, attention must be given to



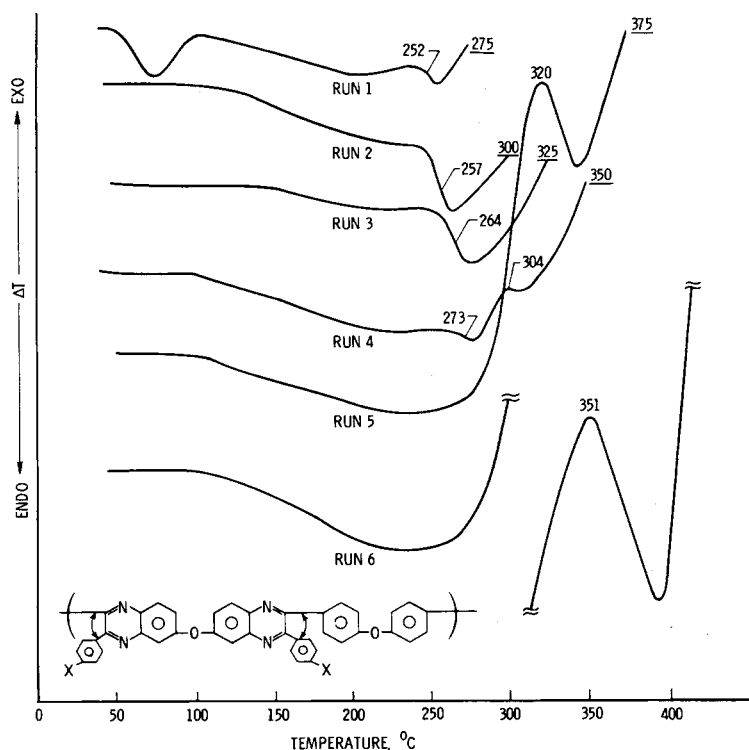


Fig. 5. Differential scanning calorimetric curves. Heating rate: 20°C/min; atmosphere: static air; sample weight: 9.3 mg; sensitivity: 0.1 mcal/s-in. X = H (70%) and C≡CØ (30%).

the presence of residual solvent, particularly *m*-cresol, an excellent plasticizer for PPQ. As demonstrated by thermogravimetric analysis, the powder samples used in this study contained <0.5% of residual solvent.

**Mechanical Properties:** Films of the PPQ void of phenylethynyl groups and those containing 5 mol % phenylethynyl groups which were stage-dried in air to 325°C and maintained at 325°C for 1 h provided the properties in Table II. The  $T_g$ 's are higher than those of the respective polymers in Table I because

TABLE II  
Thin Film Properties of PPQ<sup>a</sup>

Polymer ( $T_g$ , °C) <sup>b</sup>	Test temp (°C)	Tensile strength (psi)	Tensile modulus (psi)	Break elongation (%)
Void of C≡CØ (261)	RT	16,117	353,500	7.1
	200	7300	237,180	12.3
	232	4250	198,200	24.0
Containing 5 mol % C≡CØ (277)	RT	16,133	372,300	6.2
	200	8240	258,500	10.7
	232	6960	254,710	14.5

<sup>a</sup> Average of three specimens.

<sup>b</sup> Determined by TMA at a heating rate of 5°C/min.

of the effect of the exposure at 325°C in air. The film properties of the two materials are very similar at RT and 200°C. Pronounced differences are evident at 232°C, where the phenylethynyl containing polymer film exhibited significantly better retention of properties, apparently as a result of higher crosslink density. Films of the PPQ containing 30 mol % phenylethynyl groups prepared under the same conditions were extremely brittle. Two-mil thick films could not be cut into film specimens with a razor blade without edge irregularities which caused premature failure when tested.

The PPQ void of phenylethynyl groups and PPQ's containing 5, 10, and 30 mol % phenylethynyl groups underwent preliminary evaluation as adhesives for joining titanium (6A1-4V)-to-titanium. The adherend had a Pasa Jell 107 surface treatment. The carrier was 112 E-glass with an A-1100 finish. Cured bondline thickness ranged from 6 to 8 mils. No attempt was made to optimize bonding conditions to maximize strength. Bonding conditions were previously described in the experimental section. The tensile shear strengths at RT in Table III are respectable except for the PPQ containing 30 mol % phenylethynyl groups. This material exhibited poor flow under the bonding conditions, resulting in poor wetting. In addition, the adhesive was very brittle due to the high crosslink density. In testing of single lap shear specimens, high peel stresses are encountered which causes more brittle adhesives to fail at lower stress levels.

The increase in strength at 204°C and 232°C after 10 min for the PPQ void of phenylethynyl groups and those containing 5 and 10 mol % of phenylethynyl group after the postcure for 2 h at 371°C is attributed predominantly to the loss of residual *m*-cresol and crosslinking. Post-cured specimens from the PPQ containing 5 and 10 mol % exhibited higher 232°C strength than the PPQ void of phenylethynyl groups presumably due to more crosslinking. Aging for 1000 h at 232°C in a circulating air oven had no effect upon bond strength.

The following comments on failure pertain to all the adhesive specimens with the exception of those from the PPQ containing 30 mol % phenylethynyl groups which exhibited ~80% adhesive failure. Generally, the failure at RT and 204°C was predominantly cohesive. Thermoplastic failure was observed for most of

TABLE III  
Preliminary PPQ Ti/Ti Lap Shear Data

Polymer, PPQ	$T_g$ (°C)	Processing conditions; Final temp (°C); pressure (psi); time (h) (post-cure, h @ temp, °C)	Avg lap shear strength (psi) <sup>b</sup>			
			26°C	204°C, 10 min	232°C, 10 min	232°C, 1000 h
No C≡CØ	256	316; 200; 0.5	5150	2600	1430	1510
		316; 200; 0.5 (2 @ 371)	4930	2810	2370	—
5 mol % C≡CØ	263	316; 200; 0.5	5200	2850	1370	1250
		316; 200; 2	4730	2800	1560	1500
		316; 200; 2 (2 @ 371)	4520	3150	2720	2700
10 mol % C≡CØ	281	329; 200; 2	4840	2840	2250	2150
		329; 200; 2 (2 @ 371)	4400	3240	3100	—
30 mol % C≡CØ	ND	371; 200; 2	2380	—	2140	—

<sup>a</sup> Taken from the DSC values on Table I.

<sup>b</sup> Average of three specimens.

the unpostcured specimens at 232°C whereas the post-cured specimens tested at 232°C failed primarily cohesively. The specimens aged at 232°C for 1000 h displayed mixed failure modes with cohesive type prevailing over the adhesive mode.

Unidirectional high tensile strength graphite filament reinforced/PPQ laminates provided the mechanical properties in Table IV. No work was performed to optimize prepreg preparation or laminate fabrication. For comparison, a conventional 177°C curing epoxy system at 31% resin content with Celion-6000 as the reinforcement provided the following respective RT properties: flexural strength, flexural modulus, and short beam shear strength of 260,000, 21,000,000, and 17,000 psi. Several factors contributed to the low strength of the PPQ laminates such as the quality of the prepreg (inadequate wetting and nonuniform resin content), the rheological behavior of the PPQ at the processing temperature (viscosity high prohibiting good flow), fiber wash, and high resin content. The specimens tested at 232°C exhibited thermoplastic failure which may be due partly to the presence of residual *m*-cresol plasticizing the resin. This is suggested by the increase in short beam shear strength after a postcure for 4 h at 371°C. Thermogravimetric analysis of a laminate sample showed a weight loss of 0.3% (or ~0.9% based upon resin) up to 400°C which may be due to residual solvent. In addition, the stress-strain curves of the post-cured specimens showed a sharper break than those of the un-post-cured specimens. It is more difficult to remove residual solvent from a dense laminate than from films or adhesive specimens. Hence, the 371°C post-cure of the laminate specimens did not have as large an effect upon the mechanical properties as seen in the adhesive work.

## CONCLUSIONS

The thermally induced reaction of the pendant phenylethynyl groups cross-linked the polymers to provide higher  $T_g$ 's and better solvent resistance than

TABLE IV  
Preliminary Unidirectional Celion 6K/PPQ Laminate Properties<sup>a</sup>

Test condition	Avg flexural strength (psi $\times 10^3$ )		Avg flexural modulus (psi $\times 10^6$ )		Avg. short beam shear strength (psi $\times 10^3$ )	
	PPQ void	PPQ cont	PPQ void	PPQ cont	PPQ void	PPQ cont
	of C $\equiv$ C $\emptyset$ <sup>b</sup>	5 mol % C $\equiv$ C $\emptyset$ <sup>b</sup>	of C $\equiv$ C $\emptyset$	5 mol % C $\equiv$ C $\emptyset$	of C $\equiv$ C $\emptyset$	5 mol % C $\equiv$ C $\emptyset$
RT	204	198	19.0	18.7	11.7	11.9
204°C, 10 min	195	194	18.4	18.2	10.8	10.7
232°C, 10 min <sup>d</sup>	110	122	12.1	12.8	4.8	5.5
232°C, 10 min (post-cured, 4 h at 371°C)	—	—	—	—	6.8	7.2
232°C, 1000 h <sup>d</sup>	118	131	12.4	13.7	4.7	5.6

<sup>a</sup> Average of three specimens.

<sup>b</sup> Calculated resin content of 33%.

<sup>c</sup> Calculated resin content of 34%.

<sup>d</sup> Predominantly thermoplastic failure.

a comparable PPQ with no crosslinking groups. No discernable differences were observed in the properties of the polymers where the distribution of the phenylethynyl groups along the polymer chain was altered. Film and adhesive specimens from PPQ crosslinked via pendant phenylethynyl groups exhibited better retention of mechanical properties at elevated temperatures as compared to a comparable PPQ void of crosslinking groups.

The author gratefully acknowledges the assistance of the following people: Mrs. Alice Chang for GPC analyses, Mr. James Dezern for TBA, Mr. Robert Ely for  $\eta_{inh}$  measurements, Messrs. Phil Robinson and James Tyeryar for laminate and adhesive bond fabrication, Mr. Spencer Inge for mechanical property determination, and Mrs. Karen Whitley for TMA.

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

### References

1. P. M. Hergenrother, *SAMPE Quart.*, **3**(1), 1 (1971).
2. P. M. Hergenrother, *Polym. Eng. Sci.*, **16**(5), 303 (1976).
3. P. M. Hergenrother and D. J. Progar, *Adhesives Age*, **20**(12), 38 (1977).
4. P. M. Hergenrother and N. J. Johnston, in *Resins for Aerospace*, ACS Symposium Series 132, C. A. May, Ed., Am. Chem. Soc., Washington, D.C., 1980, p. 3.
5. P. M. Hergenrother, *Poly. Eng. Sci.*, **21**(16), 1072 (1981).
6. P. M. Hergenrother, *Appl. Polym. Symp.*, **22**, 57 (1973).
7. P. M. Hergenrother, *J. Appl. Polym. Sci.*, **18**, 1779 (1974).
8. P. M. Hergenrother, *J. Macromol. Sci., Rev. Macromol. Chem.*, **C6**(1), (1971).
9. P. M. Hergenrother, *Macromolecules*, **14**, 898 (1981).
10. M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Org. Chem.*, **28**, 2725 (1963).
11. P. M. Hergenrother, *J. Macromol. Sci. Chem.*, **A5**(2), 365 (1971).
12. R. T. Foster and C. S. Marvel, *J. Polym. Sci. A*, **3**, 417 (1965).

Received August 2, 1982

Accepted August 23, 1982