

## Quinoxaline/Phenylquinoxaline Copolymers\*

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

### Synopsis

The thermal crosslinkability of the quinoxaline moiety incorporated within poly(phenylquinoxalines) was demonstrated by differential scanning calorimetry (DSC), torsional braid analysis (TBA), and high-temperature adhesive evaluation. Several homopolymers, random copolymers, and polymer blends were prepared and evaluated. A new bis(1,2-dicarbonyl) monomer, 4-(4-phenylglyoxalylphenoxy)phenylglyoxal hydrate, was prepared and reacted with 3,3',4,4'-tetraaminobiphenyl to provide a polymer where a phenyl group was located on alternating quinoxaline rings. The apparent  $T_g$  of this polymer was initially 280°C and increased to 360°C after exposure to 400°C for 0.5 hr in air.

### INTRODUCTION

Polyquinoxalines (PQ) and poly(phenylquinoxalines) (PPQ) were first reported in 1964<sup>1,2</sup> and 1967<sup>3</sup>, respectively. Since then, a significant effort has been devoted to these polymers which have demonstrated their excellent promise for use as high-temperature structural resins.<sup>4</sup> Both systems are high-temperature thermoplastics, with the PPQ offering easier synthesis, milder processing conditions, and higher thermo-oxidative stability. Recent PPQ work has concentrated on rigidizing the polymer chain backbone,<sup>5,6</sup> and crosslinking<sup>7-9</sup> is an attempt to alleviate the high-temperature thermoplasticity. Since PQ crosslink under thermo-oxidative conditions more readily than PPQ, incorporation of quinoxaline moieties within the PPQ backbone may provide adequate crosslinking without seriously compromising the processability and thermo-oxidative stability. Therefore, a series of quinoxaline and phenylquinoxaline copolymers were prepared and their thermal crosslinkability and high-temperature adhesive properties determined as reported herein.

### EXPERIMENTAL

**3,3',4,4'-Tetraaminobiphenyl (I).** This tetraamine was obtained commercially and recrystallized from water (20g/l.) containing a pinch of sodium dithionite under nitrogen. Near-white crystals, mp 177-178°C (lit.<sup>10</sup> mp 179-180°C), were obtained in 70% recovery.

**4,4'-Oxydibenzil (II).** The dibenzil was prepared following a known proce-

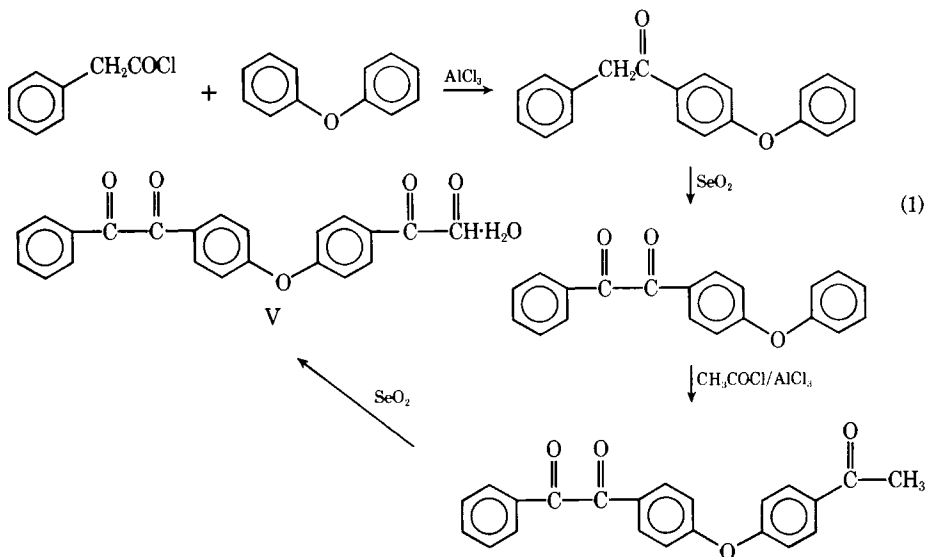
\* Presented in part at the 172nd National Meeting of the American Chemical Society, San Francisco, California, September 1976.

dure<sup>11</sup> and obtained in 66% overall yield, after recrystallization from ethanol, as yellow crystals, mp 106–107°C (lit.<sup>12</sup> mp 106.4–107.4°C).

**1,3-Bis(phenylglyoxalyl)benzene (III).** Following a known procedure,<sup>13</sup> 1,3-bis(phenylglyoxalyl)benzene was obtained in 61% overall yield, after recrystallization from ethanol, as yellow crystals, mp 98–99°C (lit.<sup>14</sup> mp 98–99.5°C).

**4,4'-Oxybis(phenyleneglyoxal hydrate) (IV).** The diglyoxal was prepared following a known procedure<sup>1</sup> and obtained as white crystals, mp 142–144°C dec. (lit.<sup>15</sup> mp 141–143°C dec.).

**4-(4-Phenylglyoxalylphenoxy)phenylglyoxal hydrate (V).** This bis-(1,2-dicarbonyl) monomer was prepared according to the reaction scheme in eq. (1):



Phenylacetyl chloride was reacted with excess diphenyl ether in the presence of anhydrous aluminum chloride in dry methylene chloride to provide 4-phenylacetyldiphenyl ether as white crystals, mp 87–88°C, in 90% yield. Oxidation was accomplished with selenium dioxide in refluxing glacial acetic acid to afford 4-phenoxybenzil as a yellow crystalline solid, mp 45–46.5°C. 4-Phenoxybenzil was acetylated in methylene chloride with acetyl chloride and anhydrous aluminum chloride to afford 4-(4-acetylphenoxy)benzil as off-white crystals, mp 93–94°C. Oxidation was performed with selenium dioxide in refluxing aqueous dioxane to afford 4-(4-phenylglyoxalylphenoxy)phenylglyoxal hydrate as a pale yellow solid. Recrystallization from aqueous dioxane gave pale-yellow crystals, mp 87–88.5°C dec. (introduced into preheated oil bath at 80°C, mp sensitive to heating rate).

ANAL. Calcd for C<sub>22</sub>H<sub>16</sub>O<sub>6</sub>: C, 70.21, H, 4.29. Found: C, 70.15; H, 4.21.

**Model Compound (VI).** As shown in eq. (2), 4-(4-phenylglyoxalylphenoxy)phenylglyoxal hydrate was reacted with 1,2-diaminobenzene in refluxing ethanol to afford a near quantitative yield of 2-[4-(4-quinoxalinyphenoxy)phenylene]-3-phenylquinoxaline:

TABLE I  
Polymer Synthesis and Characterization

Polymer no.	Polymer type	Monomers (mole) <sup>a</sup>	Solvent	Reaction conditions	$\eta_{inh}$ , dl/g <sup>b</sup>
1	Mixed	I (0.010) + V (0.010)	<i>m</i> -cresol	1 hr @ R.T., 3 hr @ 90–92°C	0.61
2	Homo PQ	I (0.030) + IV (0.030)	<i>m</i> -cresol	1 hr @ R.T., 4 hr @ 90°C	1.03
3	Homo PPQ	I (0.0297) + II (0.030)	1:1 <i>m</i> -cresol/xylene	18 hr @ R.T.	1.23
4	Co PQ:PPQ (1:1)	I (0.0588) + II (0.030) + IV (0.030)	1:1 <i>m</i> -cresol/xylene	2 hr @ 70–75°C for IV, then add II, 18 hr @ R.T.	0.65
5	Co PQ:PPQ (1:3)	I (0.0588) + II (0.015) + IV (0.045)	1:1 <i>m</i> -cresol/xylene	2 hr @ 70–75°C for IV, then add II, 18 hr @ R.T.	0.72
6	Co PQ:PPQ (1:9)	I (0.0588) + II (0.06) + IV (0.054)	1:1 <i>m</i> -cresol/xylene	2 hr @ 70–75°C for IV, then add II, 18 hr @ R.T.	0.81
7	Blend, polymers 2 and 3 (1:1)	—	1:1 <i>m</i> -cresol/xylene	2 hr @ R.T.	1.21
8	Homo PPQ	I (0.02985) + III (0.030)	1:1 <i>m</i> -cresol/xylene	18 hr @ R.T.	0.97
9	Co PQ:PPQ (1:1)	I (0.0594) + III (0.030) + IV (0.030)	1:1 <i>m</i> -cresol/xylene	2 hr @ 70–73°C for IV, then add III, 18 hr @ R.T.	0.61
10	Blend, polymers 2 and 8 (1:1)	—	1:1 <i>m</i> -cresol/xylene	2 hr @ R.T.	1.02

<sup>a</sup> See experimental section.

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

TABLE II  
 Glass Transition Temperature and Weight Loss of Polymers

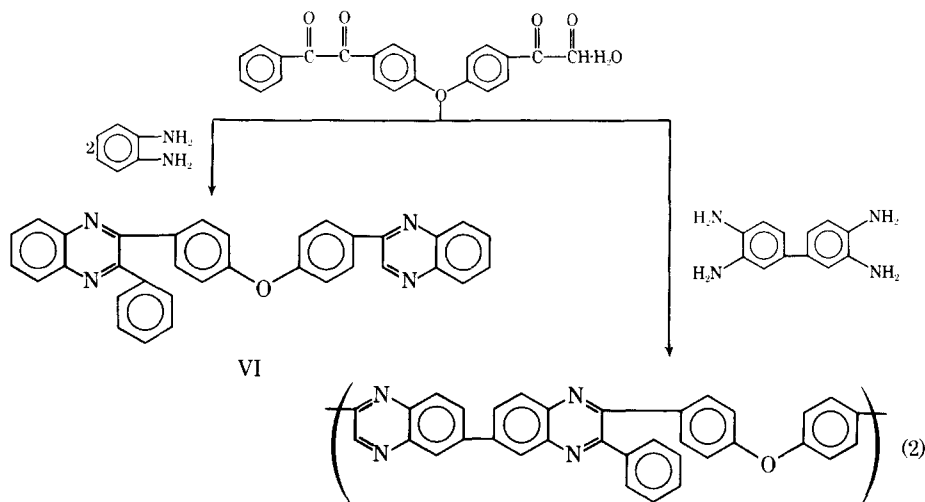
Polymer no. <sup>a</sup>	$T_g$ , °C (DSC), <sup>b</sup> after 0.5 hr @ 400°C			$T_g$ , °C (TBA), <sup>c</sup> after 0.5 hr @ 400°C			Wt. loss, %, after specified <sup>d</sup> number of hours @ 371°C in circulating air			
	Initial	In N <sub>2</sub>	In air	Initial	In N <sub>2</sub>	In air	20	48	79	105
1	289	not	detected	280	316	360	3.1	6.2	13.7	41.6
2	292	not	detected	284	308	372	7.3	44.2	93.8	—
3	293	301	318	288	297	314	3.4	5.0	14.6	44.8
4	302	not	detected	294	315	346	3.1	19.2	79.7	—
5	299	311	not detected	295	312	339	3.3	17.1	48.2	—
6	296	309	332	293	308	331	3.4	13.4	39.1	—
7	301	313	332	295	310	324	6.1	21.8	45.9	49.5
8	318	322	330	303	316	325	2.7	3.3	4.4	5.2
9	307	319	not detected	302	321	349	8.5	14.6	47.3	—
10	306	315	337	302	319	327	5.2	16.8	42.7	—

<sup>a</sup> See Table I.

<sup>b</sup>  $\Delta T = 20^\circ\text{C}/\text{min}$ ;  $T_g$  taken as inflection point of  $\Delta T$ -vs-temperature curve.

<sup>c</sup>  $\Delta T = 3^\circ\text{C}/\text{min}$ ;  $T_g$  taken at maximum damping peak (see Fig. 1).

<sup>d</sup> Weight loss on  $\sim 2$ -mil-thick films dried 2 hr at  $300^\circ\text{C}$  in air.



Recrystallization from isopropanol afforded near-white crystals, mp  $180$ – $181^\circ\text{C}$ .

ANAL. Calcd for  $\text{C}_{34}\text{H}_{21}\text{N}_4\text{O}$ : C, 81.42; H, 4.22; N, 11.17. Found: C, 81.29; H, 4.27; N, 10.98.

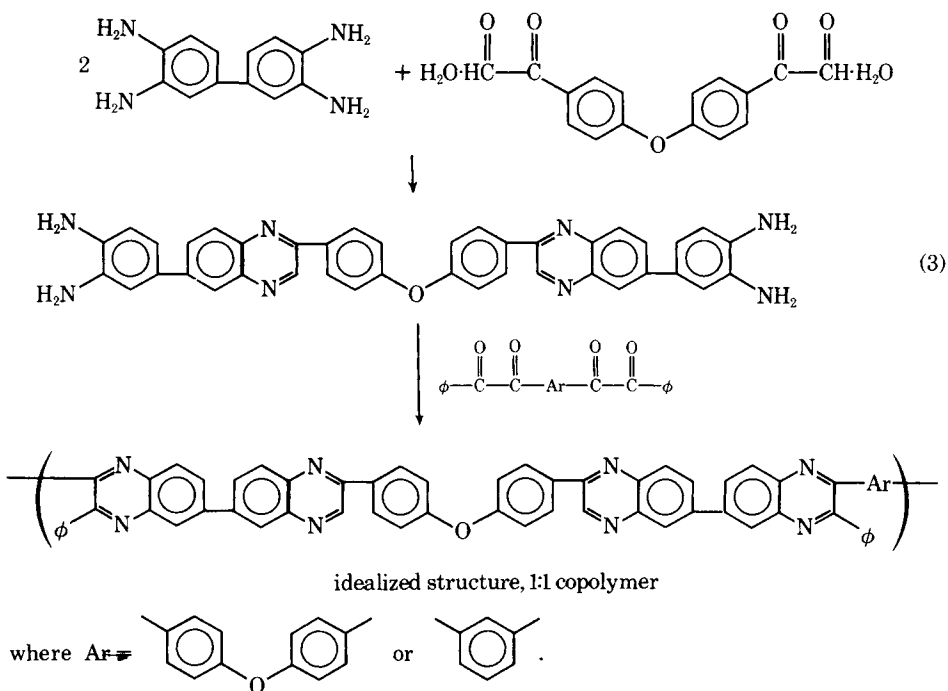
**Polymers.** As depicted in eq. (2), stoichiometric quantities of 3,3',4,4'-tetraaminobiphenyl and 4-(4-phenylglyoxalylphenoxy)phenylglyoxal hydrate were stirred in *m*-cresol (20% solids, w/v) for 1 hr at ambient temperature, followed by 3 hr at  $90$ – $92^\circ\text{C}$ . A portion of the viscous dark-amber solution was precipitated in methanol to yield a fibrous yellow solid which was thoroughly washed with hot methanol and dried at  $\sim 150^\circ\text{C}$  *in vacuo* for 4 hr. Polymer characterization is given in Table I.

The quinoxaline homopolymer was prepared by stirring stoichiometric

quantities of 4,4'-oxybis(phenyleneglyoxal hydrate) and 3,3',4,4'-tetraaminobiphenyl in *m*-cresol (18% solids, w/v) at 90°C for 4 hr. The viscous dark-red solution was poured into methanol to precipitate a yellow solid which was washed and dried as described in the preceding paragraph.

The phenylquinoxaline homopolymers were prepared following a known procedure<sup>16</sup> in a 1:1 mixture of *m*-cresol and xylene (18% solids, w/v). The stoichiometry was upset by 1.0 and 0.5 mole-% in favor of 4,4'-oxydibenzil and 1,3-bis(phenylglyoxalyl)benzene, respectively, to avoid extremely viscous solutions or gelation.

The quinoxaline and phenylquinoxaline copolymers, eq. (3),



were prepared by the following representative procedure. 3,3',4,4'-Tetraaminobiphenyl (12.5991 g, 0.0588 mole) was added to a stirred slurry of 4,4'-oxybis(phenyleneglyoxal hydrate) (9.5511 g, 0.030 mole) in a 1:1 mixture (100 ml) of *m*-cresol and xylene. The reaction mixture was stirred at 70–75°C for 2 hr and cooled to R.T. 4,4'-Oxydibenzil (13.0326 g, 0.030 mole) and solvent (40 ml) were added and the reaction mixture stirred at ambient temperature overnight to provide a viscous amber solution of copolymer. A portion of the polymer was isolated by precipitation in methanol, washed, and dried as previously described.

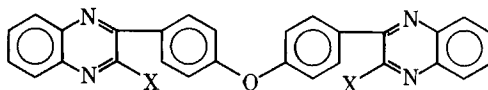
Polymer blends were prepared by dissolving 50 mole-% of the isolated PQ with 50 mole-% of the isolated PPQ in a 1:1 mixture of *m*-cresol and xylene.

**Solvents.** Practical-grade *m*-cresol and practical-grade mixed xylenes obtained from J. T. Baker Chemical Co. were used as received.

**Measurements.** The standard DSC cell with the du Pont 990 thermal analyzer and the torsional braid analyzer as described elsewhere<sup>17</sup> were used.

## RESULTS AND DISCUSSION

The polymers in Table I were prepared by the cyclopolycondensation of 3,3',4,4'-tetraaminobiphenyl with the appropriate 1,2-dicarbonyl monomer(s) in *m*-cresol or a 1:1 mixture of *m*-cresol and xylene at ~18% solids (w/v). The stoichiometry was upset in most cases by 0.5 to 1.0 mole-% in favor of bis(1,2-dicarbonyl) monomer(s) to avoid extremely viscous solutions and gelation.<sup>16</sup> In this manner, stable solutions of high molecular weight polymers were obtained. Prior to the preparation of polymer 1 (Table I), a model compound was prepared as shown in eq. (2) in an attempt to ascertain what effect a phenyl group on alternating quinoxaline rings may have upon the properties of the polymer:



X = H, mp 172°C<sup>1</sup>

X = C<sub>6</sub>H<sub>5</sub>, mp 226-227°C<sup>3</sup>

X = H and C<sub>6</sub>H<sub>5</sub>, mp 180-181°C

It was interesting to observe that the melting point of the model compound was closer to that of the corresponding unsubstituted model compound rather than the phenyl-substituted compound. However, the solubility characteristics were more similar to that of the phenyl-substituted compound.

All polymers were of sufficiently high molecular weight to cast flexible (fingernail-creasable) transparent yellow films. These were aged simultaneously in a circulating air oven at 371° ± 3°C and their weight loss recorded as a function of time. The isothermal weight loss data in Table II displayed the expected trend. The PPQ were more stable than the copolymers, which were more stable than the PQ. Polymer 1, with a phenyl group on alternating quinoxaline rings, exhibited weight losses similar to that of the corresponding random copolymer (polymer 4). In addition, the polymer blends (polymers 7 and 10) exhibited weight losses essentially identical to those of the respective copolymers (polymers 4 and 9).

The principal objective of this work was to determine if quinoxaline moieties could be incorporated within the backbone of PPQ to serve as crosslinking sites without seriously compromising the processability and thermo-oxidative stability. Such materials would be promising candidates for use as high-temperature structural resins, particularly adhesives. Polyquinoxalines readily undergo crosslinking under thermo-oxidative conditions where PPQ exhibit relatively good stability. A series of quinoxaline and phenylquinoxaline homopolymers, copolymers, and polymer blends were prepared as shown in Table I and their crosslinkability evaluated by DSC, TBA, and adhesive work.

The polymer was isolated from solution by precipitation in methanol, washed thoroughly in boiling methanol, and dried 4 hr at ~150°C *in vacuo*. The apparent glass transition temperature  $T_g$  was determined by DSC at a heating rate of 20°C/min in nitrogen, with the  $T_g$  taken as the inflection point of the  $\Delta T$ -versus-temperature curve. The  $T_g$  was determined on samples having three different thermal histories; 300°C for 0.5 hr in nitrogen; 300°C for 0.5 hr and 400°C for 0.5 hr in nitrogen; and 300°C for 0.5 hr and 400°C for 0.5 hr in static air. As shown in Table II, the  $T_g$  of certain samples could not be detected by

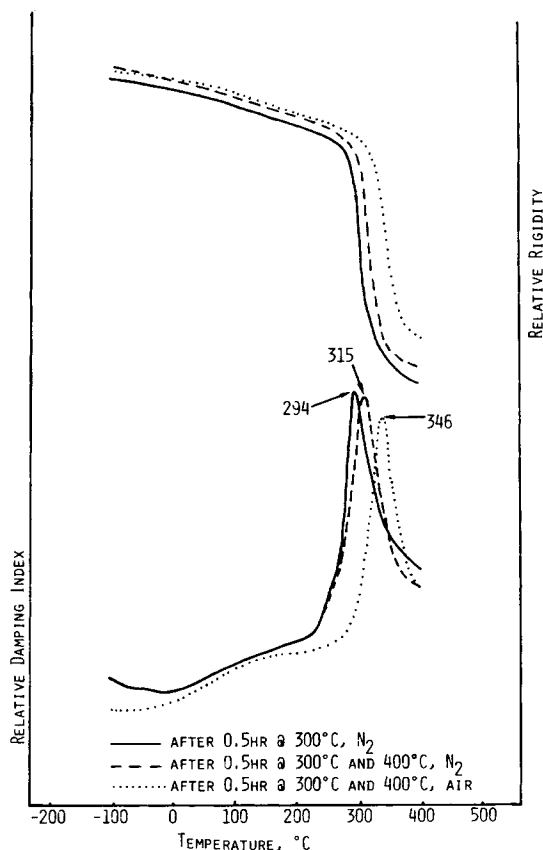


Fig. 1. Torsional braid analysis of quinoxaline/phenylquinoxaline copolymer (1:1) (polymer 4, Table I).

DSC. However, the expected trend was prevalent with samples containing the quinoxaline moiety exhibiting a greater increase in  $T_g$  after thermal and thermo-oxidative exposure than the PPQ. The polymer blends exhibited a single  $T_g$  rather than two separate  $T_g$ . A synergistic effect on  $T_g$  was observed for the copolymers (4, 5, 6, and 9), with the initial  $T_g$  by DSC and TBA being higher than the  $T_g$  of either of the homopolymers.

A mechanical method, TBA, was also employed to determine the apparent  $T_g$  of samples having the same thermal history as those used in the DSC work, except for heating rate. The  $T_g$  was taken as the temperature at the maximum damping peak at a heating rate of  $3^\circ\text{C}/\text{min}$ . Unlike DSC, TBA provided more meaningful information to substantiate that crosslinking was indeed occurring. As shown in the representative TBA curve in Figure 1, the damping peak decreased in intensity (less able to absorb damping energy due to decreased flexibility) and shifted to a higher temperature as the severity of the exposure conditions increased. In conjunction with the change in the damping peak, the relative rigidity also decreased in intensity and shifted to a higher temperature, characteristic of crosslinking. The  $T_g$  by TBA is lower than that obtained by DSC, which is expected since the sample is experiencing a mild mechanical deformation. The same trend observed in the DSC work was even more dominant

TABLE III  
Tensile Shear Strength on Titanium (6Al-4V)

Polymer no. <sup>a</sup>	Polymer type	Avg. tensile shear strength, psi <sup>b</sup>		
		R.T.	290°C, 10 min <sup>c</sup>	316°C, 10 min <sup>c</sup> (postcured <sup>d</sup> )
2	Homo PQ	3900	1700	350 (900)
3	Homo PPQ	4530	1560	300 (500)
4	Co PQ:PPQ (1:1)	4820	1630	400 (1040)
8	Homo PPQ	4440	1830	500 (550)
9	Co PQ:PPQ (1:1)	4500	1680	350 (1100)

<sup>a</sup> See Table I.

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

<sup>c</sup> Thermoplastic failure.

<sup>d</sup> Postcured 2 hr at 400°C unrestrained in air.

in the TBA work. The PQ exhibited the greatest increase in  $T_g$ , with the mixed polymer, copolymers, and polymer blends intermediate and the PPQ the lowest. After exposure at 400°C for 0.5 hr in air, all samples were insoluble in concentrated sulfuric acid, with some exhibiting swelling.

The PQ, PPQ, and copolymers were briefly evaluated as adhesives using titanium (6Al-4V) substrate having a light grit blast followed by a phosphate fluoride surface treatment. This work was performed without the benefit of process optimization and was done solely to demonstrate feasibility.

Adhesive tapes were prepared by multiple brush coating 112 type E glass having an A-1100 finish with the polymer solution until a dried tape thickness of 10–12 mils was obtained. The initial coat was a dilute solution (~5% solids) followed by several coats from the as-prepared polymer solution (~18% solids). Each coat was carefully dried at temperatures to 185°C to avoid bubbles, with a final dry of 3 hr at 185°C in air. The substrate was also primed with a dilute solution (~5% solids) of polymer, with a final dry of 3 hr at 185°C in air. Preliminary flow tests were conducted on each tape by placing a 1-in. square piece between aluminum foil in a press preheated to 399°C and applying 100 psi for 10 min. The aluminum foil sandwich was removed and the relative resin flow observed. The PPQ and the copolymers exhibited about equal flow with the PQ significantly less but still adequate for bonding.

Since the preliminary flow tests indicated adequate processability for all the polymers, fabrication conditions were held constant. Standard tensile shear specimens (ASTM D1002) were press fabricated starting at room temperature under 200 psi, increasing the temperature to 399°C under 200 psi during ~20 min, holding at 399°C under 200 psi for 20 min, and cooling under pressure. Each adhesive panel exhibited good resin flow, a tough flash, and a bondline thickness of 5–7 mils. As shown in Table III, respectable R.T. tensile shear strengths were obtained for all polymers, with the failures being primarily cohesive. Some thermoplastic failure was observed at 290°C, with pronounced thermoplastic failure apparent at 316°C.

To demonstrate the crosslinkability of the polymers containing quinoxaline units, tensile shear specimens were postcured unrestrained for 2 hr at 400°C in circulating air. The tensile shear strength of the polymers containing quin-



oxaline units more than doubled, whereas the PPQ showed only a very modest increase. Past work<sup>16,18</sup> has shown that higher strength at 290° and 316°C can be obtained by using fillers, higher temperatures, and longer times at temperature. However, the objective of the work reported in this paper was to demonstrate feasibility. Separate work may be performed to optimize the adhesive properties of the copolymers.

The assistance of Mr. George Sykes for the TBA work is gratefully acknowledged. This work was supported by NASA Grant NSG-1124 with Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061.

### References

1. G. P. deGandemaris and B. J. Sillion, *J. Polym. Sci. B*, **2**, 203 (1964).
2. J. K. Stille and J. R. Williamson, *J. Polym. Sci. B*, **2**, 209 (1964).
3. P. M. Hergenrother and H. H. Levine, *J. Polym. Sci. A-1*, **5**, 1453 (1967).
4. P. M. Hergenrother, *J. Macromol. Sci.-Rev. Macromol. Chem. C*, **6**(1), 1 (1967).
5. F. L. Hedberg and F. E. Arnold, *Amer. Chem. Soc., Div. Polym. Chem. Prepr.*, **16**(1), 677 (1975).
6. F. L. Hedberg, R. E. Arnold, and R. F. Kovar, *J. Polym. Sci., Polym. Chem. Ed.*, **12**, 1965 (1974).
7. P. M. Hergenrother, *Macromolecules*, **7**, 575 (1974).
8. R. F. Kovar, G. F. L. Ehlers, and F. E. Arnold, *Amer. Chem. Soc., Div. Polym. Chem. Prepr.*, **16**(2), 204 (1975).
9. R. T. Rafter and E. S. Harrison, *Amer. Chem. Soc., Div. Coatings Plast. Chem. Prepr.*, **35**(2), 204 (1975).
10. H. Vogel and C. S. Marvel, *J. Polym. Sci.*, **50**, 511 (1961).
11. P. M. Hergenrother, *J. Polymer Sci. A-1*, **7**, 945 (1969).
12. M. A. Ogliaruso, L. A. Shadoff, and E. I. Becker, *J. Organ. Chem.*, **28**, 2725 (1963).
13. P. M. Hergenrother and D. E. Kiyohara, *J. Macromol. Sci.-Chem.*, **A5**(2), 365 (1971).
14. W. Wrasidlo and J. M. Augl, *J. Polym. Sci. A-1*, **7**, 3393 (1969).
15. P. M. Hergenrother and D. E. Kiyohara, *Macromolecules*, **3**(4), 387 (1970).
16. P. M. Hergenrother, *J. Appl. Polym. Sci.*, **18**, 1779 (1974).
17. S. K. Dalal, G. L. Carl, A. T. Inge, and N. J. Johnston, *Amer. Chem. Soc., Div. Polym. Prepr.*, **15**(1), 576 (1974).
18. P. M. Hergenrother and H. H. Levine, *J. Appl. Polym. Sci.*, **14**, 1037 (1970).

Received June 14, 1976