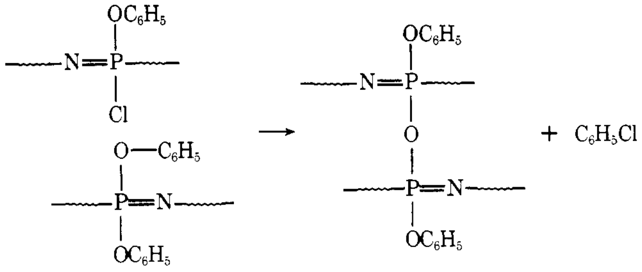
and thermal cleavage at elevated temperatures is also likely. It is possible that the initial precipitous molecular weight decline observed results from a chain cleavage process such as this.

The elimination of chlorobenzene can occur by an intra- or intermolecular interaction between residual P–Cl and P–O–C_6H_5 units (VI). Phenol could be formed by the interaction of P–OH units with P–O–C_6H_5 groupings. Traces of triphenylphosphate could presumably arise from the cleavage of polymer end units. Thus, the depolymerization mechanism is complex. High thermal stability appears to require the absence of P–Cl or P–OH units along the chain and the absence of acids in the polymer matrix. Presumably, the presence of crosslinks would also interfere with the depolymerization process.



VI

Finally, some indirect evidence exists that the depolymerization may take place in two steps: first by a cleavage of chains at weak points (Cl, OH, NH, or branch points), followed by a second process which involves a cyclization depolymerization initiated from the ends of the linear fragments. A comparison of the intrinsic viscosity curves shown in Figure 1 with the gpc curves shown in Figure 2 suggests that the initial rapid decrease in intrinsic viscosity coincides with a rather sharp transposition of the main gpc peak from $\bar{M}_n \approx 1.7 \times 10^6$ to $\bar{M}_n \approx 6.5 \times 10^4$. (This is especially evident in the gpc curves obtained for the depolymerizations carried out at 150–250°.) This behavior is consistent with a fragmentation of the initial polymer molecules into, on the average, 20 to 30 fragments. Subsequently, the low molecular weight cyclic oligomers ($\bar{M}_n \approx 1 \times 10^3$) make their appearance in the gpc curves. If this mechanism is correct, approximately one initial chain cleavage site should be present for every 300 repeating units (or one for every 100 trimer molecules originally converted to $(NPCl_2)_n$). However, microanalysis of the poly(diphenoxyphosphazene) indicated that the residual chlorine content of the polymer was approximately eight times higher than this (one chlorine atom per 39 repeating units). Thus, the suspicion exists that below 250° the depolymerization process is initiated mainly by OH or NH units or at branch points along the chain. Presumably, the destabilizing influence of chlorine becomes important mainly at the higher temperatures (300–400°) where chlorobenzene elimination occurs.

Acknowledgment. We thank the U. S. Army Research Office, Durham, for the support of this work.

References and Notes

(1) This paper is Part XX in a series of phosphorus-nitrogen compounds.
(2) Part XIX: H. R. Allcock and W. J. Cook, *Macromolecules*, **7**, 284 (1974).
(3) H. R. Allcock, "Phosphorus-Nitrogen Compounds," Academic Press, New York, N. Y., 1972.
(4) H. R. Allcock, *Chem. Rev.*, **72**, 315 (1972).
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(8) H. R. Allcock and G. Y. Moore, *Macromolecules*, **5**, 231 (1972).
(9) H. R. Allcock, D. P. Mack, and W. J. Cook, *Inorg. Chem.*, **11**, 2584 (1972).
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(13) G. Allen, C. J. Lewis, and S. M. Todd, *Polymer*, **11**, 44 (1970).
(14) G. Allen and R. M. Mortier, *Polymer*, **13**, 253 (1972).
(15) Mass spectra were obtained with the use of an A.E.I. MS 902 instrument. Samples were injected as liquids.
(16) G. L. Hagnauer and N. S. Schneider, *J. Polym. Sci., Part A-2*, **10**, 699 (1972).
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Poly(phenyl-*as*-triazines) and Poly(phenylquinoxalines). New and Cross-Linked Polymers[1]

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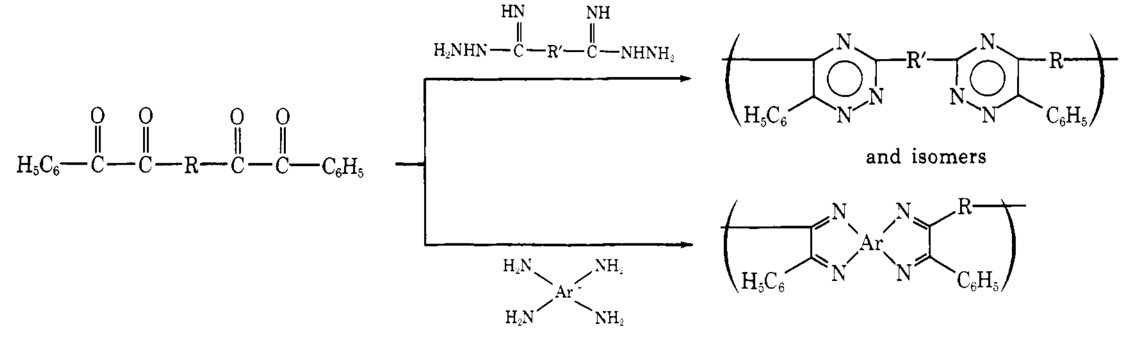
ABSTRACT: Several new, high molecular weight, soluble poly(phenyl-*as*-triazines) (PPT) and poly(phenylquinoxalines) (PPQ) were prepared where various substituents were placed in the para position of the pendant phenyl group attached to the heterocyclic ring. The effect which these substituents had upon the properties (*e.g.*, T_g) of the polymer was determined. Preliminary work was performed where reactive groups were introduced within the polymer which could undergo a latent cross-linking reaction without the evolution of volatiles to reduce the thermoplasticity of these polymers at elevated temperatures. The T_g of several PPT and PPQ containing cyano or cyanato groups increased significantly or could not be detected after exposure to 400°. The cyano and cyanato groups apparently undergo trimerization to form *sym*-triazine cross-links. A cyano-containing PPQ provided tensile shear strengths on the Ti adherend at *RT* of 3500 psi, at 316°, of 1500 psi which increased to 2100 psi after a postcure at 371° for 1 hr.

Poly(phenyl-*as*-triazines) (PPT) and poly(phenylquinoxalines) (PPQ) are high performance heterocyclic polymers which are potentially useful in functional and structural applications. These two families of polymers are very similar in their method of preparation, processability, and overall properties except for the difference in use temperature. The PPT exhibit long term (*e.g.*, >1000 hr) performance at temperatures as high as 260°, whereas the PPQ exhibit long term stability at temperatures as high as 316°. Poly(phenyl-*as*-triazines) and PPQ are generally prepared from the reaction of phenyl-substituted bis(1,2-dicarbonyl) compounds with diamidrazones and aromatic bis(*o*-diamines), respectively, as shown in eq 1.



(1)

R = arylene or alkylene, R′ = nil or 2,6-pyridinediyl, Ar = aromatic

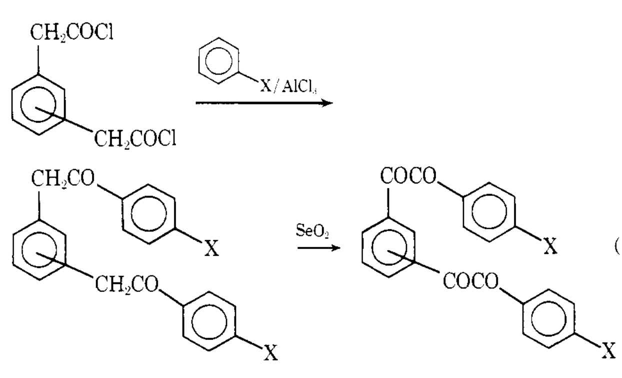
Poly(phenyl-*as*-triazines) were first reported in 1969,[3] additional work was disclosed later,[4] and a patent was issued in 1973.[5] Whereas, PPQ's were first reported in 1967[6] and since then a significant effort has been devoted to their synthesis,[7-17] mechanical evaluation,[11,15,16,18-20] and thermal characterization.[21-24] Two patents[25,26] were issued which include PPQ.

These polymers are soluble in high molecular weight form in solvents such as *m*-cresol or chloroform and exhibit good processability relative to other high temperature polymers. The processability comes by virtue of their thermoplasticity which is desirable for fabrication but detrimental for structural use at elevated temperature.

The work presented herein concerns the preparation and characterization of several new polymers where various substituents are located on the pendant phenyl group attached to the heterocyclic ring. This work was performed to determine how these substituents affected the properties of the polymers. In addition, preliminary work was performed where reactive groups were introduced within the polymer which could undergo crosslinking reaction to reduce the thermoplasticity of these polymers at elevated temperature.

Results and Discussion

Monomers. The various phenylene bis(1,2-dicarbonyl) monomers (compounds no. 1–8) in Table I were prepared according to the reaction scheme in eq 2 following a slight modification of a known procedure[8]



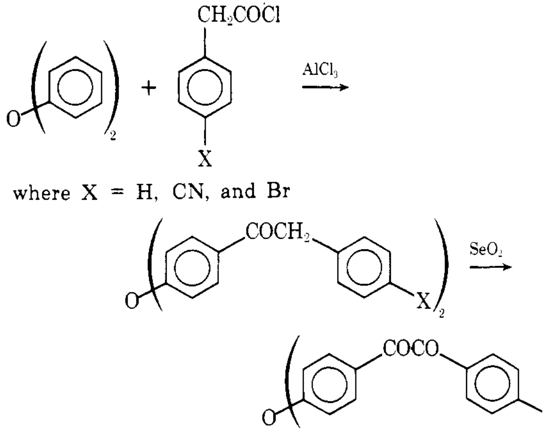
(2)

where X for the para isomer = H only; and X for the meta isomer = H, C_2H_5, C_4H_9, OCH_3, OC_6H_5, OPhCN, and C_6H_5.

m-Bis(*p*′-hydroxyphenylglyoxylyl)benzene (compound no. 9, Table I) was obtained by the demethylation of *m*-bis(*p*-methoxyphenylglyoxylyl)benzene (compound no. 5) with hydrogen bromide in acetic acid.

The diphenyl ether bis(1,2-dicarbonyl) monomers (compounds no. 10–12 in Table I) were prepared similarly following a known procedure[1] as shown in eq 3.

The other monomers used in polymer formation were oxalamidrazone for the PPT and 3,3′,4,4′-tetraaminobenzophenone or 3,3′-diaminobenzidine for the PPQ. Oxalamidrazone was prepared as previously described[4c] by the addition of hydrazine to cyanogen. The two aromatic tetraamines were obtained commercially and recrystallized as previously reported[15] prior to use in polymer formation. Characterization of these monomers is presented in Table II.

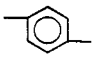
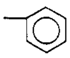
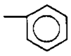
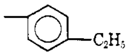
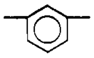
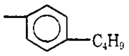
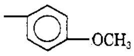
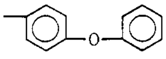
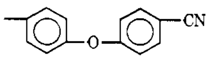
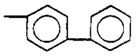
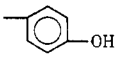
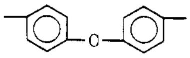
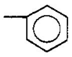
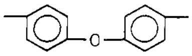
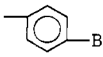
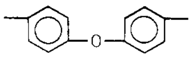
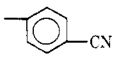

where X = H, CN, and Br

(3)

Polymers. The PPT and PPQ reported in Tables III–IV were prepared in relatively high molecular weight form by cyclopolycondensation of oxalamidrazone or an aromatic bis(*o*-diamine) with a bis(1,2-dicarbonyl) compound in a 1:1 mixture of *m*-cresol and xylene except for polymers no. 7-T, 7-Tc, 7-Q, and 7-Qc. In the preparation of polymers no. 7-T and 7-Q, only *m*-cresol was employed as solvent. To prepare polymers no. 7-Tc and 7-Qc the precursor hydroxy containing polymer was treated in DMAC with cyanogen bromide and triethylamine. Clear yellow tough flexible films were readily cast from all polymer solutions. For characterization work, each polymer in Tables III–VI was isolated by quenching in methanol in a Waring blender, thoroughly washed with methanol, and dried at 130° over phosphorus pentoxide for 4 hr *in vacuo*. The thermal history of each polymer was essentially identical, thereby permitting a meaningful comparison of T_g's. However, the molecular weights differed as indicated by the inherent viscosity. This is known[15] in PPQ to cause substantial variations in certain polymer properties such as the T_g's. The T_g's reported in Tables III–VI were determined by differential scanning calorimetry at $\Delta T = 20°C/min$ in N_2 with the T_g taken as the inflection point of the ΔT *vs.* temperature curve.

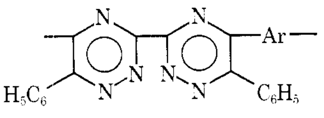
The three factors which govern the T_g are molecular flexibility, molecular symmetry, and intermolecular association (*e.g.*, polar interaction and hydrogen bonding). Each of these factors is apparent in the trend of the T_g's of PPT

Table I
Bis(1,2-dicarbonyl) Compounds

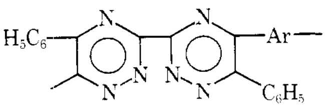
Compd	XOCOC–Ar–COCOX				Elemental analysis[b]	
no.	Ar	X	Mp, °C[a]	Formula	%C	%H
1			125–126 (125–126, ref 27)	$C_{22}H_{14}O_4$		
2			98.5–99.5 (98–99.5, ref 8)	$C_{22}H_{14}O_4$		
3			53.5–54.5	$C_{26}H_{22}O_4$	78.23 (78.37)	5.51 (5.57)
4			37–38	$C_{30}H_{30}O_4$		
5			116.5–117.5	$C_{24}H_{18}O_6$	71.52 (71.63)	4.47 (4.51)
6			131–132 (131.5–132.5, ref 16)	$C_{34}H_{22}O_6$		
7			139.5–141.5	$C_{36}H_{20}N_2O_6$	75.03 (74.99)	3.43 (3.49)
8			176–177.5	$C_{34}H_{22}O_4$	82.43 (82.57)	4.47 (4.49)
9			204–205	$C_{22}H_{14}O_6$	70.47 (70.58)	3.71 (3.77)
10			106.5–107.5 (106.4–107.4, ref 28)	$C_{28}H_{18}O_5$		
11			192–193	$C_{28}H_{16}Br_2O_5$	56.71 (56.78)	2.63 (2.72)
12			194–196	$C_{30}H_{16}N_2O_5$	74.28 (74.37)	3.36 (3.33)

[a] Literature melting point in parentheses. [b] Theoretical values in parentheses.

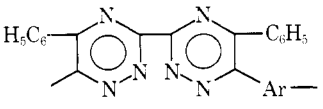
and PPQ. For example, flexibilizing groups such as ethyl, butyl, methoxy, or phenoxy introduced in the para position of the pendant phenyl group lower the T_g. Indroduction of another phenyl group in this position increases the T_g. The increase in the T_g for the hydroxy substituted PPT (polymer no. 7-T, Table III) and the hydroxy substituted PPQ (polymer no. 7-Q, Table IV) is apparently due to strong intermolecular association through hydrogen bonding. The increase in the T_g of the cyano substituted PPT (polymer no. 10-T, Table III) and the cyano substituted PPQ (polymer no. 11-Q, Table IV) is apparently due to a combination of two factors: polar interaction and increased molecular symmetry (*e.g.*, a more regular configuration and, accordingly, a more perfect conformation). The increase in molecular symmetry is proposed on the following basis. As indicated in eq 1 and as previously discussed[4a,11] three isomers can be present in the mer units of PPT or PPQ. For example, the following isomers could be present in a PPT.



-5,5′-isomer



-5,6′-isomer



-6,6′-isomer

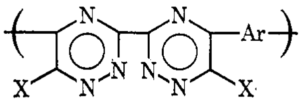
The presence of isomers has been used to explain the excellent solubility, processability, and amorphicity (absence of long range periodicity) of PPT and PPQ (*e.g.*, ref 22). If the difference in reactivity of the 1,2-dicarbonyl groups in the tetracarbonyl monomer can be altered considerably, the possibility of obtaining more of a predominance of one isomer is favored. This should be possible with *p,p*′-oxybis(*p*″-cyanobenzil) (compound no. 12, Table I). The electron withdrawing power of the cyano group increases the reactivity of the carbonyl group adjacent to the *p*-cyanophenyl group, while the ether oxygen donates electrons to the other carbonyl, thereby decreasing its reactivity. As a result, the increase in the T_g of the cyano-substituted PPT and PPQ [prepared from *p,p*′-oxybis(*p*″-cyanobenzil)] may be due partially to increased molecular symmetry as well as polar interaction from the cyano group.

Table II
Oxalamidrazone and Aromatic Bis(*o*-diamines)

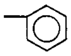
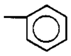
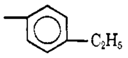
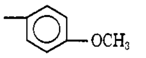
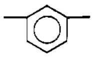
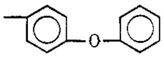
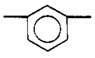
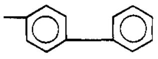
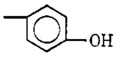
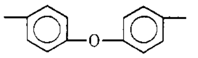
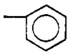
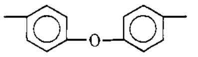
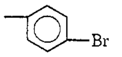
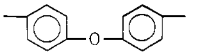
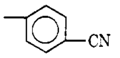
Compd	Mp, °C	Lit. mp, °C
Oxalamidrazone	178–179 dec	179–180 dec[4c]
3,3′-Diaminobenzidine	177–178	179–180[29]
3,3,′4,4′-Tetraamino-benzophenone	216–217	217[30]

Cross-Linking Studies. Poly(phenyl-*as*-triazines) and PPQ are high temperature thermoplastics which is desirable for fabrication but detrimental for structural use at high temperatures. The thermoplasticity can be reduced through high temperature postcure which induces some cross-linking, presumably through thermal and/or thermal-oxidative degradation resulting in improved high temperature performance (*e.g.*, less thermoplasticity) but at the sacrifice of lowering the use life at elevated temperature. An alternate route is to introduce cross-linking into these polymers *via* latent cross-linking sites. This route permits the polymerization to proceed to soluble processable polymers which can then undergo thermally or catalytically induced reaction without the evolution of volatiles to provide

Table III
Characterization of Poly(phenyl-*as*-triazines)



A

Polymer no.	Ar	X	Concn,[a] % solids	Soln vis,[b] Hz	η_{inh},[c] dl/g	T_g, °C[d]
1-T			9.5	7,000	2.02	313
2-T			9.5	1,500	0.89	268
3-T			20	1,000	0.40	232
4-T			20	1,900	0.60	253
5-T			20	1,000	0.50	215
6-T			20	1,000	0.45	273
7-T			20	24,000	0.64[f]	337
8-T[e]			14	2,700	1.01	258
9-T			15	3,500	0.72	317
10-T			20	25,400	1.34	293

[a] Concentration based upon weight of reactants and volume of solvent (1:1 mixture of *m*-cresol and xylene except for polymer no. 7-T, only *m*-cresol used as solvent). [b] Brookfield viscosity at 25°. [c] Inherent viscosity, 0.5% *m*-cresol solution at 25°. [d] Glass transition temperature, determined by differential scanning calorimetry at ΔT = 20°C/min in N_2. [e] Stoichiometry upset by ~1.0% in favor of *p,p'*-oxydibenzil to avoid gelling. [f] 0.5% DMAC solution at 25°.

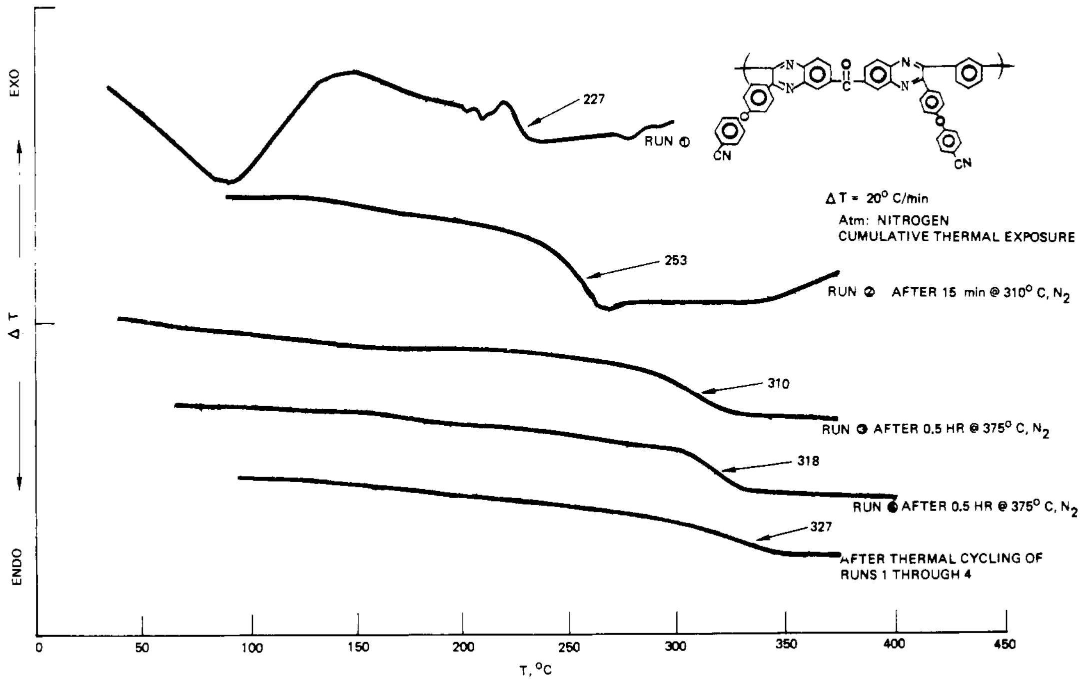
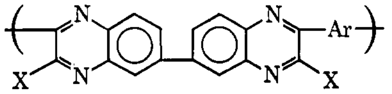


Figure 1. Differential scanning calorimetry of poly-2,2'-(*m*-phenylene)-6,6'-carbonylbis[3-(*p*'-cyanophenoxyphenyl)quinoxaline].

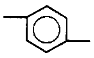
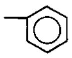
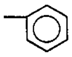
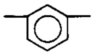
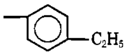
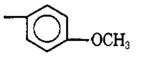
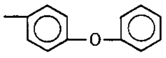
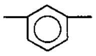
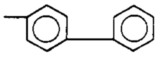
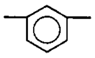
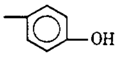
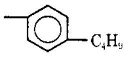
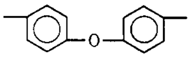
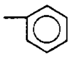
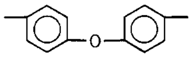
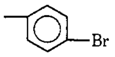
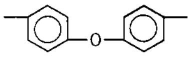
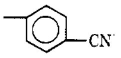
cross-linking, thereby reducing the thermoplasticity of these polymers. The preliminary work reported herein was directed toward this goal.

The T_g's of several PPT and PPQ initially and after cycling to 350° and 400° respectively in nitrogen are reported in Tables V and VI. Since more dramatic changes were observed in the PPQ series, perhaps due to the higher exposure temperature, further discussion on the increase in T_g is confined to PPQ. The PPT series were not exposed to 400° because their thermal decomposition temperature by thermogravimetric analysis is ~400°.[4b] The T_g's of the phenylquinoxaline polymers which contained cross-linking groups (OCN and CN) increased significantly after cycling to 400° in nitrogen. Whereas the T_g's of similar PPQ which

Table IV
Characterization of Poly(phenylquinoxalines)

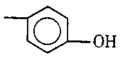
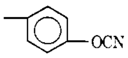
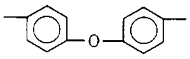
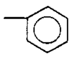
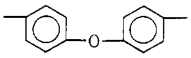
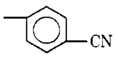
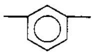
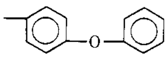
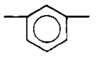
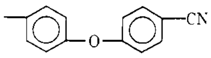


B

Polymer no.	Ar	X	Concn,[a] % solids	Soln vis,[a] Hz	η_{inh},[a] dl/g	T_g, °C[a]
1-Q[b]			18	52,000	1.32	351
2-Q[b]			17	2,500	0.73	319
3-Q			20		0.64	288
4-Q			20		0.64	305
5-Q			20		0.45	245
6-Q			14.2		0.81	326
7-Q[b]			10	6,500	1.10[d]	375
8-Q			20		0.49	231
9-Q[c]			17.3	18,500	1.19	290
10-Q			16		1.10	313
11-Q			10		1.62	340

[a] See Table I for description. [b] Prepared in *m*-cresol. [c] Stoichiometry upset by ~1.0% in favor of the bis(1,2-dicarbonyl) compounds to avoid gelling. [d] 0.5% DMAC solution at 25°.

Table V
Characterization of Standard and Cross-Linked PPT

Polymer no.	A: Ar	A: X	η_{inh},[a] dl/g	T_g, °C[a]: Initial	T_g, °C[a]: After 0.5 hr at 350° in N_2
7-T[b]			0.64	337	339
7-T$_c$			0.60	No T_g detected	
8-T[b]			1.01	258	261
10-T[b]			1.34	293	303
5-T[b]			0.50	215	216
5-T$_c$			0.47	211	247 (279)[c]

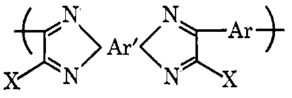
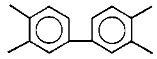
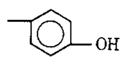
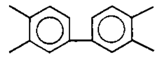
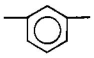
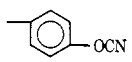
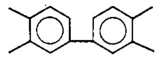
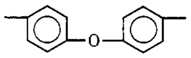
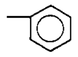
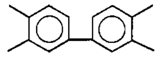
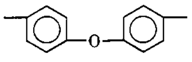
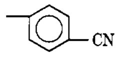
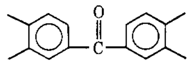
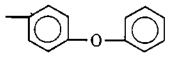
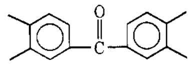
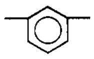
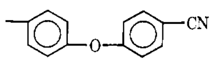
[a] See Table I for definition. [b] Polymers previously numbered and reported in Table I. [c] Blended with catalytic amount of *p*-toluenesulfonic acid.

did not contain potential cross-linking groups increased only a few degrees upon cycling to 400° in nitrogen.

The T_g of PPQ-OH (polymer no. 7-Q) was 379° after cycling to 400°, whereas no T_g could be detected for PPQ-OCN (polymer no. 7-Qc). The PPQ-OH was treated with cyanogen bromide to transform the hydroxyl groups to cyanato groups. The infrared spectrum of the resulting polymer indicated a high degree of substitution as evidenced by medium intense absorptions in the 4.35 to 4.5μ-region characteristic of cyanato groups. The infrared spectrum of the PPQ-OCN sample after cycling to 400° in nitrogen showed only very weak absorptions at 4.35 to 4.5 μ presumably due to trimerization of the cyanato groups to *sym*-triazines (cyanurates). In addition, the 400° exposed sample failed to dissolve in *m*-cresol or even concentrated sulfuric acid. Trimerization of cyanato compounds to cyanurates has been studied by Grigat[31] and is being used as a polymer forming reaction.[32]

Although the trimerization of aromatic nitriles to *sym*-triazines is generally conducted in the presence of strong

Table VI
Characterization of Standard and Cross-Linked PPQ

Polymer no.	 C			η_{inh},[a] dl/g	T_g, °C[a]	
	Ar′	Ar	X		Initial	After 0.5 hr at 400° in N_2
7-Q[b]				1.10	375	379
7-Q_c				1.17	No T_g detected to 450°	
8-Q[b]				1.19	290	294
11-Q[b]				1.62	340	371
12-Q				0.72	215	218
12-Q_c				0.51	227	327

[a] See Table I for definition. [b] Polymers previously numbered and reported in Table II. [c] Elemental Analysis. Calcd for $(C_{49}H_{26}N_3O_6)_n$: C, 78.81; H, 3.51; N, 11.26. Found: C, 78.76; H, 3.62; N, 11.11 (as prepared).

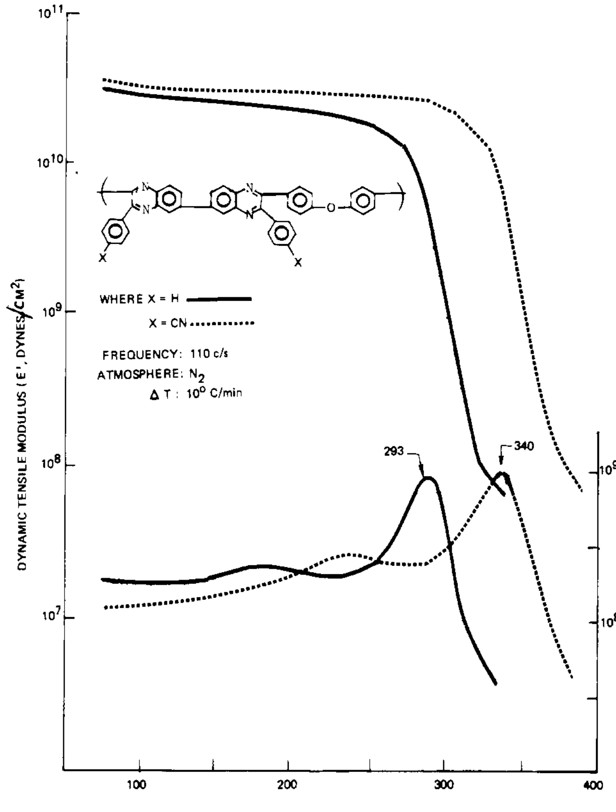


Figure 2. Dynamic mechanical relaxation spectra of PPQ.

acids (*e.g.*, chlorosulfonic acid) or under high pressure (*e.g.*, 7500 atm), certain aromatic nitriles (*e.g.*, *o*-hydroxybenzonitrile[33]) can be thermally converted to *sym*-triazines. Therefore, cyano groups were incorporated in PPQ in an attempt to obtain cross-linking through the formation of *sym*-triazines. In Table VI, the T_g of polymer no. 11-Q was initially 340° and increased to 371° after cycling to 400° in nitrogen. The infrared spectrum of the 400° exposed sample showed a slight decrease in the intensity of the nitrile absorption at 4.5 μ. In addition, the 400° exposed sample became insoluble in concentrated sulfuric acid.

To enhance the reactivity of an aromatic nitrile to trimerize to *sym*-triazine an electron donating group was placed in the para position to it as shown in polymer no. 12-Qc (Table VI). This polymer initially exhibited a T_g of 227°, which increased to 327° after exposure to 400° in nitrogen. The increase in T_g as a function of thermal exposure is shown in Figure 1.

The infrared spectrum of the 400° exposed sample showed a significant decrease in the intensity of the nitrile absorption at 4.5 μ presumably due to trimerization to *sym*-triazine. The trimerization of the cyano groups can be enhanced by various catalysts. A catalytic amount of *p*-toluenesulfonic acid was blended with polymer no. 12-Qc and the T_g determined. Initially the T_g was 227° and increased to 321° after 0.5 hr at 350° in nitrogen. Further work on the use of catalysts to enhance trimerization of the cyano group and the use of other groups to provide cross-linking will be reported later.

In addition to DSC measurements, characterization work on many of the polymers reported herein included dynamic mechanical relaxation measurements using the Vibron viscoelastomer (Model DDV-II) equipped with a high temperature furnace,[22] elongation behavior of films, and thermal penetration of moldings. The latter two methods used the Du Pont Thermomechanical Analyzer. The dynamic mechanical relaxation spectra of two PPQ are shown in Figure 2. The maximum dispersion peak for the cyano-containing PPQ occurred at 340° whereas the noncyano-containing PPQ exhibited a peak at 293°. Film elongation behavior of these two PPQ (Figure 3) showed the cyano containing PPQ exhibited a drastic change in the slope at 338° whereas the noncyano-containing polymer displayed pronounced elongation at 291°. By thermal penetration (Figure 4) of small moldings, the slope of the cyano-substituted PPQ curve began to change at 275° with the major change occurring at 327°, while the slope of the noncyano PPQ began to change at 220° with the major change occurring at 285°. The results of these methods verified the T_g values obtained by DSC.

Mechanical Properties. Standard tensile shear specimens were fabricated using stainless steel (PH 17-7) adherend having a phosphate fluoride surface treatment with unfilled tape prepared by solution coating 112-A1100 car-

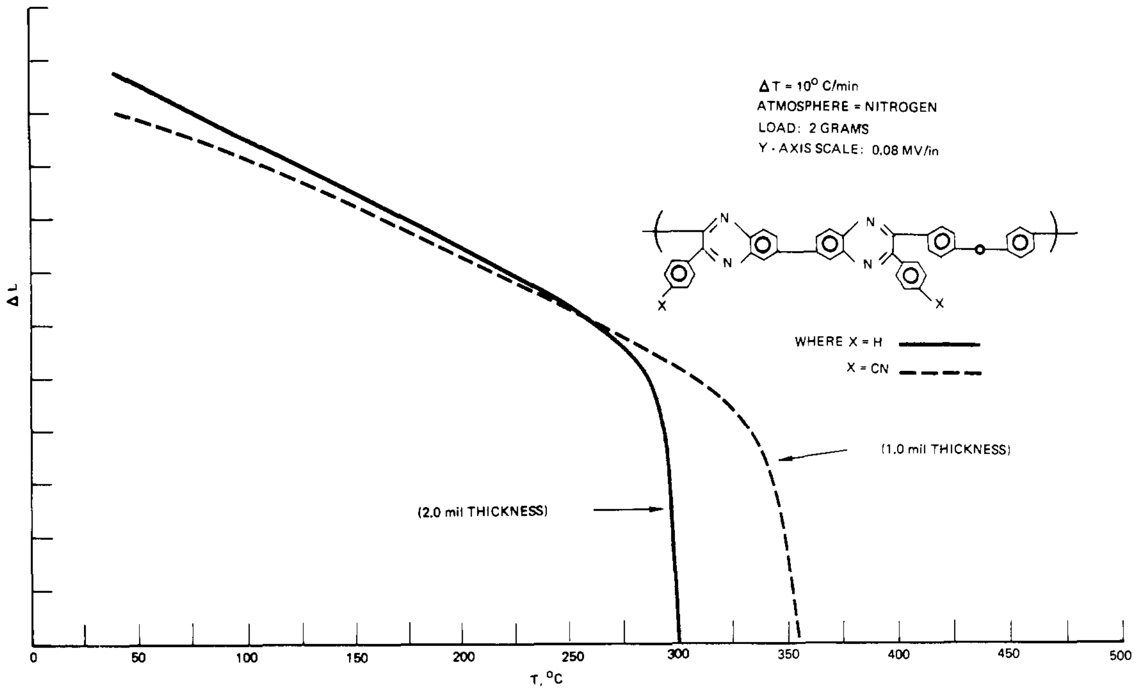


Figure 3. Elongation behavior of PPQ films.

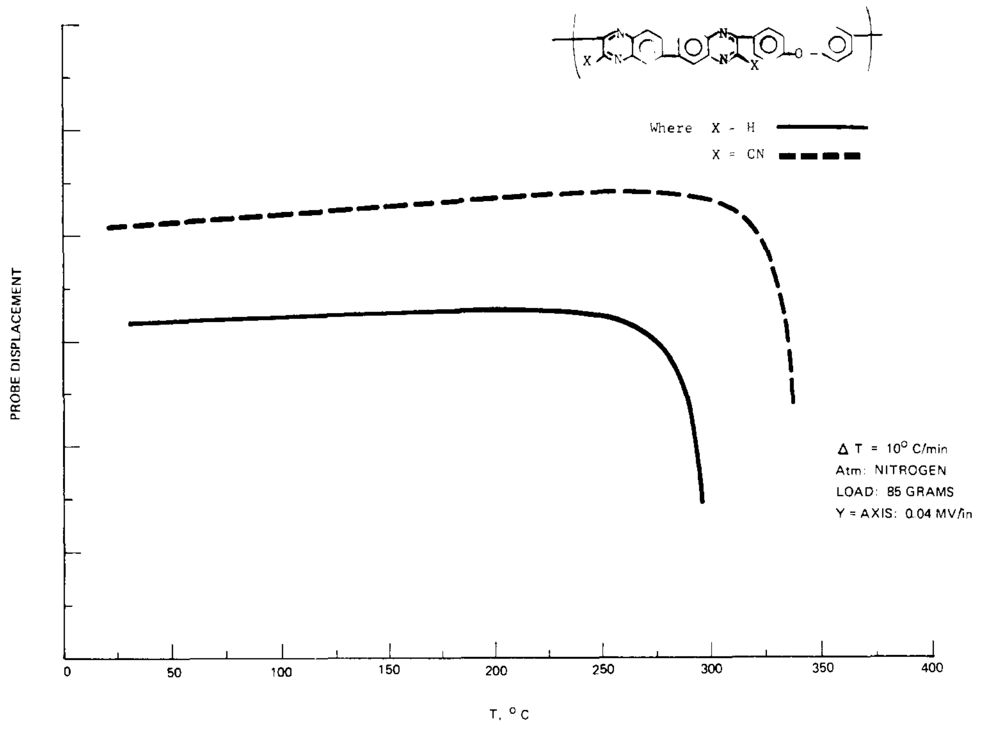


Figure 4. Thermal penetration of PPQ moldings.

rier with polymer no. 12-Qc (Table IV) and drying to a total volatile content of 0.20% (9 mils thick). The adhesive panels were fabricated in a press starting at *RT* to 316° (600°F) during 1 hr, at 316° for 1 hr, and at 371° (700°F) for 1 hr under 50 psi in nitrogen. The resulting specimens provided the following tensile shear strengths: *RT* of 3500 psi and 316° after 10 min at 316° of 1500 psi. After a postcure of 1 hr at 371° in air, the 316° strength increased to 2100 psi. Under these fabricating conditions, the 316° bond strengths are the highest ever reported for a PPQ. Generally, PPQ adhesive specimens fabricated under these conditions provide 316° strength of <800 psi due to pronounced thermoplastic failure. This preliminary work demonstrated the potential which this route offers to improve the structural performance of PPQ at elevated temperature.

Experimental Section

Since the experimental procedures for the preparation of the bis(1,2-dicarbonyl) compounds are similar, the synthesis of two representative monomers is presented.

***m*-Bis(*p*′-hydroxyphenylglyoxylyl)benzene (Compound No. 9, Table I).** A solution of the diacid chloride of *m*-phenylenediacetic acid (69.0 g, 0.30 mol) and anisole (138 g, 1.28 mol) in carbon disulfide (250 ml) was added dropwise during 2 hr to a stirred slurry of anhydrous aluminum chloride (98 g, 0.74 mol) in carbon disulfide at 8 to 12°. After complete addition, the dark red reaction mixture was stirred at ambient temperature for 18 hr followed by slowly pouring onto ice and hydrochloric acid with stirring. Methylene chloride (∼200 ml) was used to rinse out the reaction flask and also poured onto the ice. The organic phase was separated, washed twice with cold water, dried over drierite, and concentrated. The residual tan solid was washed in a Waring blender twice with *n*-hexane and dried to yield the intermediate diketone in 92% yield (102 g), mp 82–84°. *m*-Bis(*p*′-methoxyphenacyl)benzene (103 g, 0.27 mol) and selenium dioxide (61.5 g, 0.55 mol) were refluxed in glacial acetic acid (1 l.) for 6 hr. The black reaction mixture was filtered hot and the red filtrate treated with charcoal and refiltered. Upon cooling, a yellow solid (70.4 g, 72% yield), mp 112–114°, separated which was recrystallized from ethanol (1.5 l.) to afford *m*-bis(*p*′-methoxyphenylglyoxylyl)benzene as yellow fluffy crystals (38.5 g, 55% yield), mp 116.5–117.5°. *m*-Bis(*p*′-methoxyphenylglyoxylyl)benzene (47.8 g, 0.12 mol) was dissolved in glacial acetic acid (500 ml) and aqueous hydrobromic acid (47–48%, 150 ml) was added. The reaction mixture was refluxed for 22 hr followed by pouring the cooled light red solution into ice water (1 l.). The resulting yellow precipitate was isolated, washed with water, and dissolved in aqueous potassium hydroxide solution (50 g in 1 l. of H_2O). Filtration provided a clear red solution which was neutralized with hydrochloric acid to provide an orange gum. Upon washing in hot water, the orange gum turned yellow and solidified to yield a yellow solid (40.8 g) which sintered at 184°, wet at 190°, and cleared at 200°. The yellow solid was boiled in water (1.5 l.) and ethanol added (∼300 ml) until a clear solution formed. Filtration provided a yellow solution which was partially cooled (∼45–50°) and refiltered. Upon cooling, a yellow amorphous solid formed which was again recrystallized from the water–ethanol (5:1) mixture. *m*-Bis(*p*′-hydroxyphenylglyoxylyl)benzene was obtained as a yellow solid (11 g, 25% yield from the demethylation step), mp 204–205°.

***p*,*p*′-Oxybis(*p*″-bromobenzil) (Compound No. 11, Table I).** A solution of the acid chloride of *p*-bromophenylacetic acid (73.7 g, 0.33 mol) and diphenyl ether (27.2 g, 0.16 mol) in *sym*-tetrachloroethane (TCE, 100 ml) was added during 1.2 hr to a stirred slurry of anhydrous aluminum chloride (53.2 g, 0.40 mol) in TCE (160 ml) at 7 to 10°. After complete addition, the reddish-brown reaction mixture was stirred at ambient temperature for 18 hr followed by pouring onto ice and hydrochloric acid. Methylene chloride was added to aid in separation and the organic phase washed twice with water. After drying over drierite, the organic phase was concentrated to 150 ml volume and poured into hexane. The resulting white solid was washed thoroughly with *n*-hexane and dried. Recrystallization of the white solid (83 g, mp 180–183°) from benzene (2.8 l.) afforded the intermediate diketone as a white crystalline solid (63 g, 57% yield), mp 186.5–188.5°. The intermediate diketone (56.4 g, 0.10 mol) and selenium dioxide (22.2 g, 0.20 mol) were refluxed in glacial acetic acid (900 ml) for 18 hr. Benzene (600 ml) was added and the hot black reaction mixture filtered. Upon cooling, a yellow solid separated, which was isolated and recrystallized from benzene to provide *p*,*p*′-oxybis(*p*″-bromobenzil) as a yellow solid (42.3 g, 71.5% yield), mp 192–193°.

Polymers. The polymers reported in Tables III–VI, except for polymers no. 7-Tc and 7-Qc in Table V and VI, were prepared by adding the bis(1,2-dicarbonyl) monomer as a powder to a stirred slurry of the other monomer in *m*-cresol or a 1:1 mixture of *m*-cresol and xylene. The resulting reaction mixture was stirred for 18 hr at ambient temperature to provide a viscous solution. To obtain polymers no. 7-Tc and 7-Qc the precursor hydroxy polymer was treated with cyanogen bromide and triethylamine in dry DMAC.

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