References and Notes

(1) Exploratory Ring-Opening Polymerization. 9. For the previous paper in this series, see: Cho, I.; Kim, J.-B. *J. Polym. Sci., Polym. Lett, Ed.*, in press.

(2) Zambelli, A.; Natti, G.; Sacchi, C.; Crain, W. O., Jr.; Roberts, J. D. *Macromolecules* **1971**, *4*, 475. Natti, G.; Dall'Asta, G.; Pasquon, I.; Valvassori, A.; Zambelli, A. *J. Am. Chem. Soc.* **1961**, *83*, 3343. Khlok, D.; Deslandes, Y.; Prud'homme, J. *Macromolecules* **1976**, *9*, 809.

(3) Richards, D. H.; Scilly, N. F. *Chem. Commun.* **1968**, 1515. Inoue, H.; Helbig, M.; Vogl, O. *Macromolecules* **1977**, *10*, 1331. Weil, G.; Vogl, O. *Polym. Bull.* **1978**, *1*, 181.

(4) Bailey, F. E.; Henry, J. P.; Lunderberg, R. D.; Whelan, J. M. *J. Polym. Sci., Part B* **1964**, *2*, 447. Taketa, M.; Endo, R.; Matsuura, Y. *J. Polym. Sci., Part C* **1968**, *23*, 487. Bassi, I. W.; Scordamaglia, R. *Makromol. Chem.* **1973**, *166*, 283. Crawley, S.; MaNeill, I. C. *J. Polym. Sci., Polym. Chem. Ed.* **1978**, *16*, 2593.

(5) Starkweather, H. W., Jr. *J. Polym. Sci., Polym. Phys. Ed.* **1973**, *11*, 587. Morisaki, S. *Nippon Kagaku Kaishi* **1979**, 364.

(6) Otsu, T.; Aoki, S.; Nakatani, R. *Makromol. Chem.* **1970**, *134*, 331. Tanaka, T.; Vogl, O. *J. Macromol. Sci., Chem.* **1974**, *A8*, 1059.

(7) Tanaka, T.; Vogl, O. *Polym. J.* **1974**, *6*, 522.

(8) Murayama, N.; Amagi, Y. *J. Polym. Sci., Part B* **1966**, *4*, 115, 119. Richards, D. H.; Scilly, N. F.; Williams, F. J. *Chem. Commun.* **1968**, 1285. Richards, D. H.; Scilly, N. F.; Williams, F. J. *Polymer* **1969**, *10*, 603, 611. Atkinson, J.; MacCallum, J. R. *Eur. Polym. J.* **1972**, *8*, 809, 819, 833. Sakaguchi, Y.; Omori, A.; Omura, H. *Kobunshi Kagaku* **1972**, *29*, 15. Otsu, T.; Ishikawa, T. *Polym. Prepr., Jpn.* **1978**, *27*, 98. Matsumoto, A.; Iwanami, K.; Oiwa, M. *J. Polym. Sci., Polym. Lett. Ed.* **1980**, *18*, 211. Quach, L.; Otsu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 2377, 2391, 2405. Quach, L.; Otsu, T. *Ibid.* **1982**, *20*, 2501.

(9) Stille, J. K.; Chung, D. C. *Macromolecules* **1975**, *8*, 114.

(10) Longley, R. I., Jr.; Emerson, W. S.; Blardinelli, A. J. "Organic Synthesis"; Wiley: New York, 1963; Collect. Vol. IV, p 311.

(11) Longley, R. I., Jr.; Emerson, W. S. *J. Am. Chem. Soc.* **1950**, *72*, 3079.

(12) Stille, J. K.; Oguni, N.; Chung, D. C.; Travin, R. F.; Aoki, S.; Kamachi, M. *J. Macromol. Sci., Chem.* **1975**, *A9*, 745. Nishida, S.; Moritani, I.; Teraji, T. *J. Org. Chem.* **1973**, *38*, 1878. Williams, J. K.; Wilex, D. W. McKusick, B. C. *J. Am. Chem. Soc.* **1962**, *84*, 2210. Hall, H. K., Jr.; Ykman, P. *Ibid.* **1975**, *97*, 800. Hall, H. K., Jr.; Dunn, L. C.; Padias, A. B. *J. Org. Chem.* **1980**, *45*, 835. Abdelkader, M.; Hall, H. K., Jr.; *Ibid.* **1982**, *47*, 292. Hall, H. K., Jr.; Abdelkader, M. *Ibid.* **1981**, *46*, 2948.

(13) Hall, H. K., Jr.; Rasoul, H. A. A.; Gillard, M.; Abdelkader, M.; Nogues, P.; Sentman, R. C. *Tetrahedron Lett.* **1982**, *23*, 603. Rasoul, H. A. A.; Hall, H. K., Jr. *J. Org. Chem.* **1982**, *47*, 2080.

(14) Snider, B. B.; Routh, D. M.; Killinger, T. A. *J. Am. Chem. Soc.* **1979**, *101*, 6023.

(15) Smith, C. W.; Norton, D. G.; Ballard, S. A. *J. Am. Chem. Soc.* **1951**, *73*, 5267.

(16) Kamio, K.; Meyersen, K.; Schulz, R. C.; Kern, W. *Makromol. Chem.* **1966**, *90*, 187.

(17) Cho, I.; Lee, J.-Y. *Macromolecules* **1983**, *16*, 150.

(18) Levy, G. C.; Nelson, C. L. "Carbon-13 Nuclear Magnetic Resonance for Organic Chemists"; Wiley-Interscience: New York, 1972.

(19) Tanaka, T.; Vogl, O. *J. Macromol. Sci., Chem.* **1974**, *A8*, 1299.

Fire- and Heat-Resistant Laminating Resins Based on Maleimido-Substituted Aromatic Cyclotriphosphazenes

Devendra Kumar,[†] George M. Fohlen, and John A. Parker*

Chemical Research Projects Office, NASA, Ames Research Center,
Moffett Field, California 94035. *Received October 4, 1982*

ABSTRACT: A novel class of flame- and heat-resistant polymers has been synthesized by the thermal polymerization of maleimido-substituted aromatic cyclotriphosphazenes. The polymer obtained from tris(aminophenoxy)tris(maleimidophenoxy)cyclotriphosphazene has good thermal stability and is noteworthy for its high char yield, viz., 82% at 800 °C in nitrogen and 81% at 700 °C in air. Graphite-fabric laminates prepared with this polymer did not burn in pure oxygen (limiting oxygen index 100%), even at 300 °C, and were tested for mechanical properties. Hexakis(4-maleimidophenoxy)cyclotriphosphazene and some fluorine-containing monomers have also been synthesized. The structures of these cyclic phosphazene precursors and polymers were characterized by FT IR spectrophotometry, ^{1}H NMR, ^{19}F NMR, and ^{31}P solid-state magic angle spinning NMR spectroscopy, and mass spectrometry. The curing behavior of the polymer precursors and the thermal stabilities of the polymers were evaluated by differential scanning calorimetry (DSC) and thermogravimetric analyses (TGA).

Introduction

Considerable interest exists in the use of high-strength lightweight composites for the construction of both new and retrofitted aerospace vehicles. These composites are made by embedding various types of fibers or fabrics in a resin matrix. The polymer used for such a matrix is most commonly an epoxy resin, although other resins such as phenolic, poly(ether sulfone), poly(phenyl sulfone), and bismaleimide resins have also been used for certain applications.

Graphite–epoxy composites, however, suffer disadvantages where structural integrity and fire retardancy at higher temperatures are of prime importance. This is more or less true with other resin systems also. Many of these resins burn to give smoke and toxic gases and also have processing problems.

The principal objective of the present work is to provide greatly improved new fire- and heat-resistant binders having high anaerobic char yields useful for reinforced composites.

Inherent in our approach is the synergism of the phosphorus–nitrogen combination in respect to fire retardation[1] and the fact that this combination, especially when in the form of phosphazene, does not form toxic products upon oxidative thermal decomposition.[2] In addition, the maleimido substitution on the cyclotriphospazene ring has been made in view of our[3] recent work with bismaleimides and the fact that this would result in polymers having high anaerobic char yields.[4]

Several high-temperature polymers based on cyclotriphosphazenes have been reported in the literature,[5,18] but few have been used for composites. In another series,

---

[†] NRC-NASA Research Associate, 1981–1983. Permanent address: 28, Vijay Block, Shakarpur Extension, Delhi-110092, India.

0024-9297/83/2216-1250\$01.50/0 © 1983 American Chemical Society

Scheme I

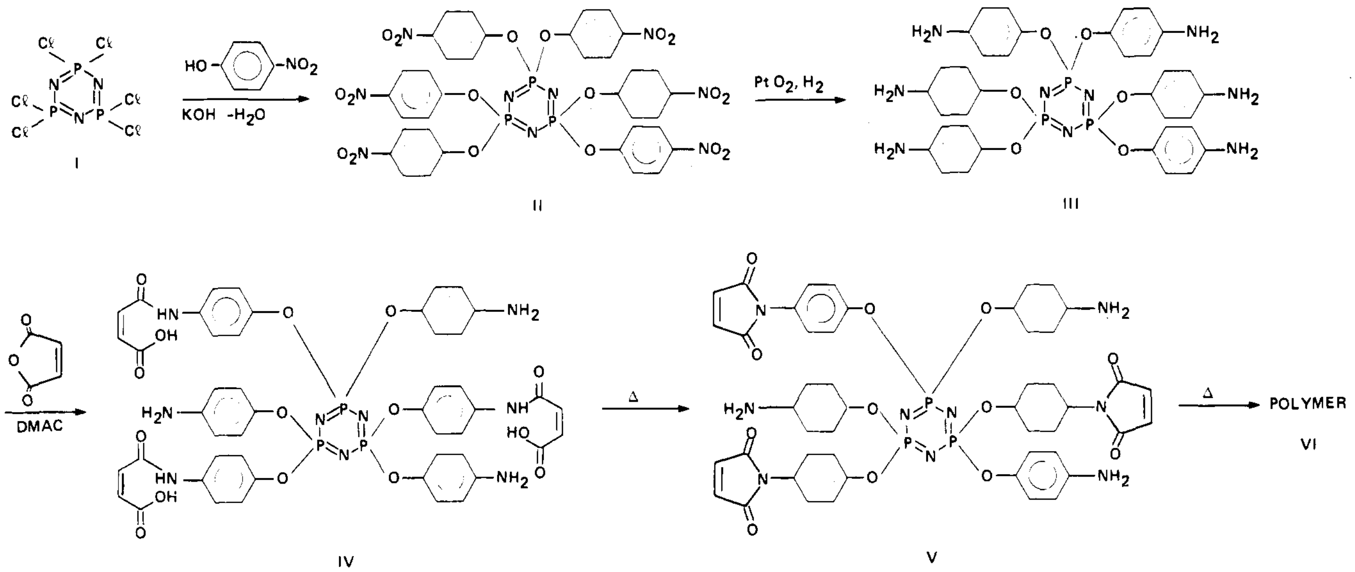


Table I
Elemental Analytical Data

compd		% C	% H	% N	% P	% F
II	calcd	44.65	2.49	13.08	9.65	
	found	44.78	2.58	12.80	9.88	
III	calcd	55.17	4.63	16.09	11.87	
	found	55.17	4.73	15.98	12.09	
IV	calcd	53.49	3.89	11.70	8.64	
	found	54.11	4.07	11.46	8.82	
V	calcd	56.30	3.52	12.33	9.10	
	found	56.20	3.72	12.21	8.99	
VI	calcd	56.30	3.52	12.33	9.10	
	found	56.02	3.88	12.03	8.97	
VII	calcd	52.52	3.50	9.19	6.78	
	found	52.37	3.86	9.22	6.53	
VIII	calcd	57.00	2.85	9.98	7.36	
	found	56.50	3.01	10.09	7.91	
XI	calcd	48.67	1.63	8.52	6.29	15.41
	found	48.07	1.82	8.50	6.46	15.78

various heterocyclic phosphorus-containing polymers derived from phosphine oxide have also been reported[6,7] having good fire-resistant properties.[7]

We here report the synthesis of novel maleimido-end-capped aromatic cyclotriphosphazene precursors that are capable of thermal polymerization to give improved fire- and heat-resistant polymers. Laminates using graphite cloth have been made, and some physical and thermal properties are presented.

Results and Discussion

Syntheses and Characterization of Cyclotriphosphazene Polymer Precursors. The overall reaction sequences for the syntheses of aromatic-substituted and fluoroaromatic-substituted cyclotriphosphazenes are outlined in Schemes I and II.

Hexakis(4-aminophenoxy)cyclotriphosphazene[8,9] (III) was synthesized from hexachlorocyclotriphosphazene (I) and 4-nitrophenol followed by reduction[9] of the hexakis-nitro compound (II).[8]

Figure 1 shows the 100-MHz ^{1}H NMR of maleamic acid IV in dimethylacetamide. The exchangeable three-proton (H_A) singlet at 10.80 ppm was assigned to maleamic acid protons and the broad nine-proton (H_B) singlet at 8.00 ppm was assigned to maleamido and aromatic amino protons. The observation of double doublets at 7.65 and 7.55 and at 7.00 and 6.99 ppm, each corresponding to six aromatic protons (H_C and H_D), indicates the reaction of the three terminal amino groups with maleic anhydride. The latter is further substantiated by the fact that the rest of the

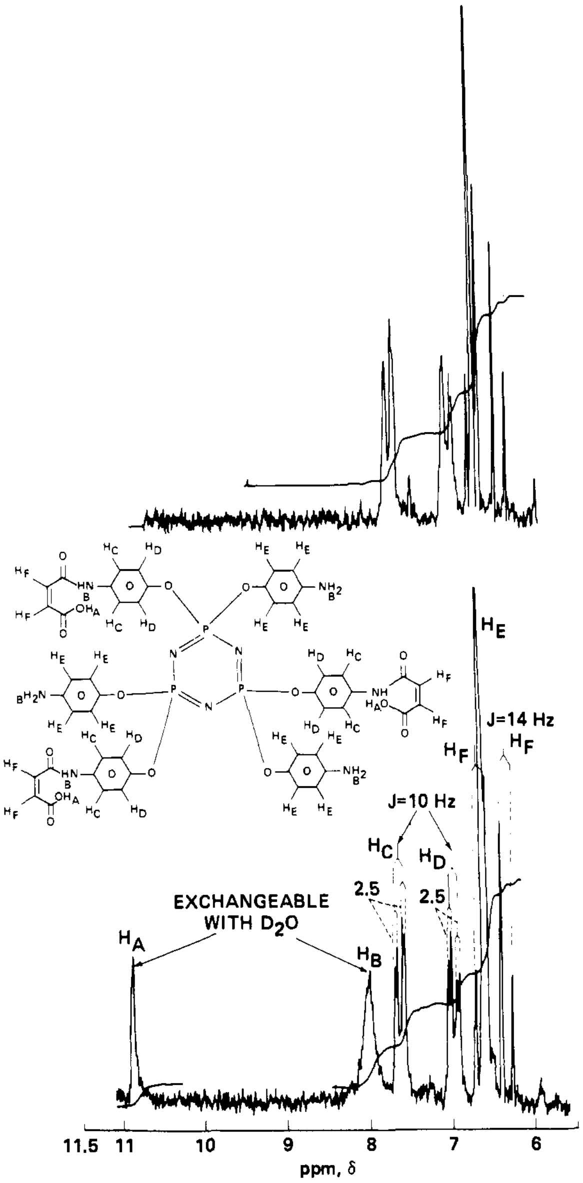
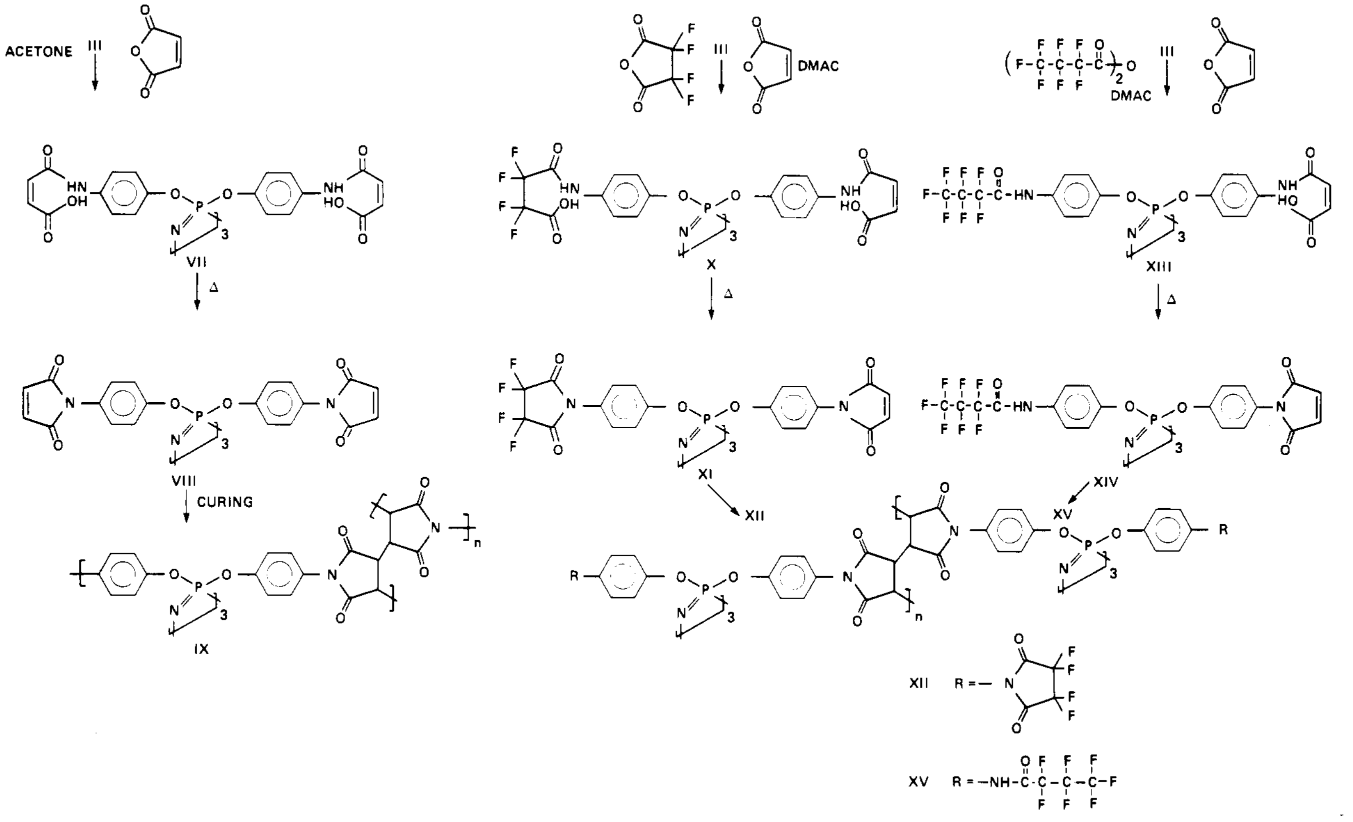


Figure 1. Proton nuclear magnetic resonance spectra of IV: (top trace) in DMAC: (bottom trace) after addition of D_2O drops.

Scheme II



twelve aromatic protons (H_E) resonate as a singlet at 6.60 ppm, similar to that observed in the parent hexakis(4-aminophenoxy)cyclotriphosphazene (III). The reaction of three of the six available amino groups has been further confirmed by the observation of the six-proton quartet (H_F) at 6.70–6.25 ppm, corresponding to the *cis*-olefinic protons. The observation of amino groups downfield is an indication of their hydrogen bonding with neighboring carbonyls. The condensation of maleic anhydride with aromatic amino groups attached to different phosphorus atoms of the cyclotriphosphazene ring is preferred here because of stereochemical considerations and can be substantiated by the symmetrical pattern observed in the ^{1}H NMR of the aromatic protons.

The infrared spectrum of the maleamic acid IV (Figure 2a) indicates that the parent cyclotriphosphazene ring is intact in this compound. The band at 1630 cm^{-1} is interpreted as the deformation mode of the NH_2 groups. Heating the DMAC solution of maleamic acid IV for about 1 h at 160–165 °C gave the maleimide V. Its infrared spectrum (Figure 2b) is compatible with this structure.

Reaction of hexakis(4-aminophenoxy)cyclotriphosphazene (III) with maleic anhydride at ambient temperature in dry acetone gave the hexakis(maleamic acid) VII, which was confirmed by ^{1}H NMR and IR analysis. Heating a DMAC solution of this maleamic acid at refluxing temperature (170–180 °C) for 2.5 h afforded hexakis(4-maleimidophenoxy)cyclotriphosphazene (VIII). An intense singlet at 7.20 ppm in its ^{1}H NMR spectrum with the disappearance of *cis*-olefinic quartet indicated the formation of maleimido groups. Its IR spectrum showed the presence of imide carbonyls, olefinic groups, and aromatic groups along with the cyclotriphosphazene ring.

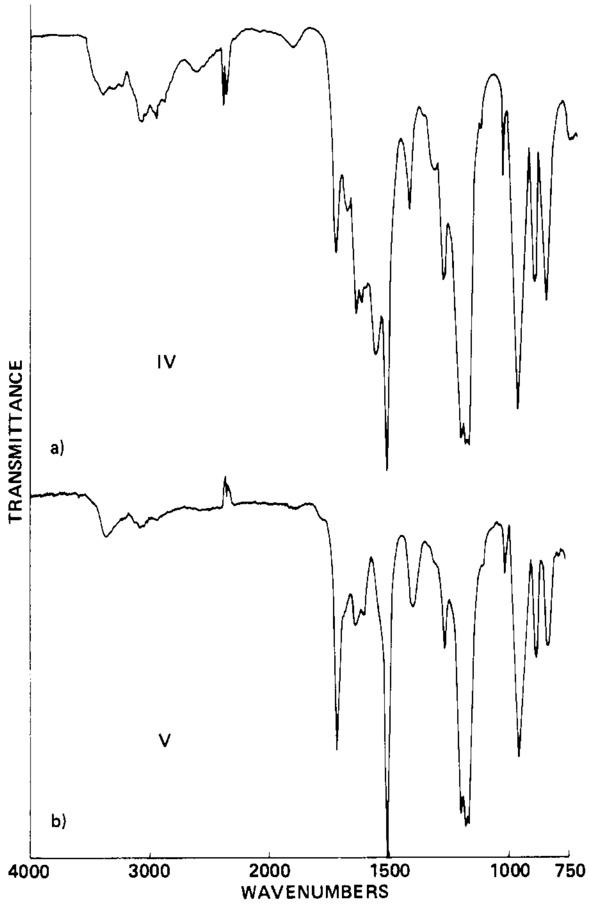


Figure 2. Infrared spectra of (a) IV on NaCl disk. (b) V on NaCl disk.

In another series, hexakis(4-aminophenoxy)cyclotriphosphazene (III) was reacted in part with tetrafluorosuccinic anhydride in DMAC. The subsequent addition of the required amount of maleic anhydride gave the fluorinated maleamic acid X. Its ^{1}H NMR spectrum showed a six-proton quartet (6.65–6.20 ppm) along with two D_2O-exchangeable singlets each comprising six protons (11.05 and 10.70 ppm) corresponding to the *cis*-olefinic

Table II
Decomposition Temperatures and Char Yields of Polymers VI, IX, and XII

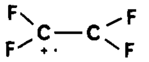
	in N_2			in air			
						char yield, %	
polymer	PDT, °C	PDT_{max}, °C (W^a)	char yield, % 800 °C	PDT, °C	PDT_{max}, °C (W^a)	800 °C	700 °C
VI	380		82	380	770 (73)	65	81
IX	395	420 (93)	76	395	420 (93) 770 (59)	50	75
XI	380	395 (90)	65	380	530 (70) 760 (50)	42	60

[a] W = residue at indicated temperature.

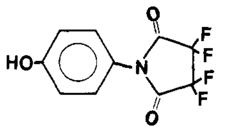
bond and the acid and amido groups, respectively, indicating that all six protons have undergone reaction, three being substituted with maleic anhydride. This has further been substantiated by the observation of 24 aromatic protons as two separated multiplets at 7.73–7.45 and 7.10–6.90 ppm.

Tetrafluorosuccinic anhydride was selected because its reactivity is similar to that of maleic anhydride. The fluorine content is expected to increase toughness and flame retardancy in the polymer. Solvents such as tetrahydrofuran, dioxane, ether, and xylene were also tried for this reaction, but is was found that DMAC provided the cleaner desired partial reaction.

Heating the DMAC solution of X in a nitrogen atmosphere at 150–160 °C and finally at the refluxing temperature (170–180 °C) gave the maleimide XI. The indicated temperatures were critical to obtain XI. The progress of the reaction was monitored by ^1H NMR. Observation of an intense singlet at 7.12 ppm corresponding to maleimido olefinic protons along with the closely spaced multiplet indicated the completion of cyclodehydration reaction. The presence of fluorine was seen from the ^{19}F NMR, IR, and elemental analysis. The 1675-cm^{-1} band in the IR spectrum of XI indicates that a small amount of isoimide formation has also taken place. The presence of the tetrafluorosuccinimido moiety in the maleimide XI may further be confirmed by the observation in its mass spectrum of the following fragments:



m/e 100



m/e 263

A similar set of reactions was performed by reacting III with heptafluorobutyric and maleic anhydrides to give the corresponding maleic acid XIII and maleimide XIV. The structures of XIII and XIV were consistent with their ^1H NMR and IR spectra.

Polymerization of Cyclotriphosphazene Maleimides. A solution of cyclotriphosphazene maleimide V in DMAC in a shallow dish was placed in a circulating-air oven at 160–162 °C for 0.25 h; it was then heated at 232–233 °C for 1–1.5 h and at 285 °C for 0.5 h. A tough dark brown polymer (VI) was obtained. Maleimides VIII and XI were similarly polymerized to IX and XII, respectively. Figure 3 shows the DSC curve in nitrogen for maleimide VIII. A similar DSC pattern was observed for monomers V and XI. Fluorinated cyclotriphosphazene maleimide XIV on polymerization, however, gave a brittle polymer (XV).

The thermal stabilities of polymers VI, IX, and XII were investigated by dynamic thermogravimetric analyses in air and nitrogen atmospheres. The analytical data are shown in Figure 4. The polymer decomposition temperatures (PDT), the temperatures at which the polymers' maximum rate of weight loss occurred (PDT_{max}), and the char yields, in both air and nitrogen, are summarized in Table II. The results show that the threshold temperature at which major fragmentation occurs is 380–400 °C in both air and nitrogen, with maximum thermooxidative decomposition taking place mainly beyond 700 °C in air in all the polymers.

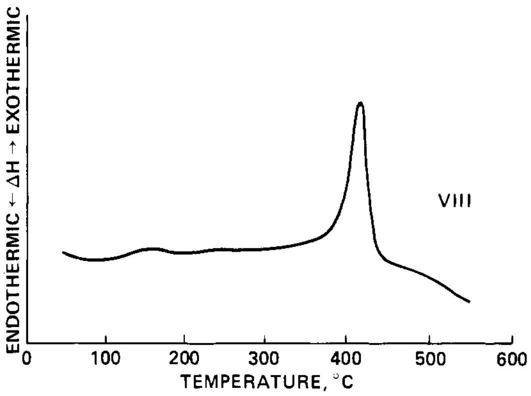


Figure 3. Differential scanning calorimetry scan of VIII. Conditions: atmosphere, N_2; heating rate, 10 °C/min; N_2 flow, 100 mL/min.

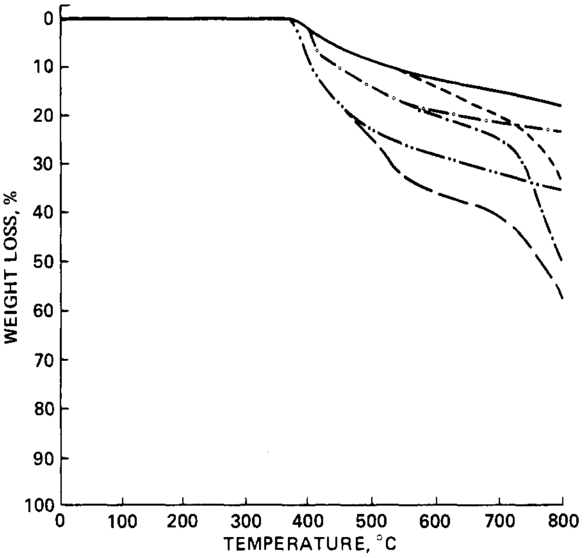


Figure 4. Thermogravimetric analysis of (—) VI in N_2, (- - -) VI in air, (-∘-) IX in N_2, (-·-) IX in air, (-··) XII in N_2, and (— — —) XII in air. Conditions: gas flow rate, 100 mL/min; heating rate, 10 °C/min.

It is interesting to note that these thermosetting polymers show higher char yields in nitrogen and particularly in air than most of the bismaleimides and other known polymers that are presently in use for composite fabrication. Polymer VI showed char yields of 82% at 800 °C in nitrogen and 81% at 700 °C in air. Similar high char was

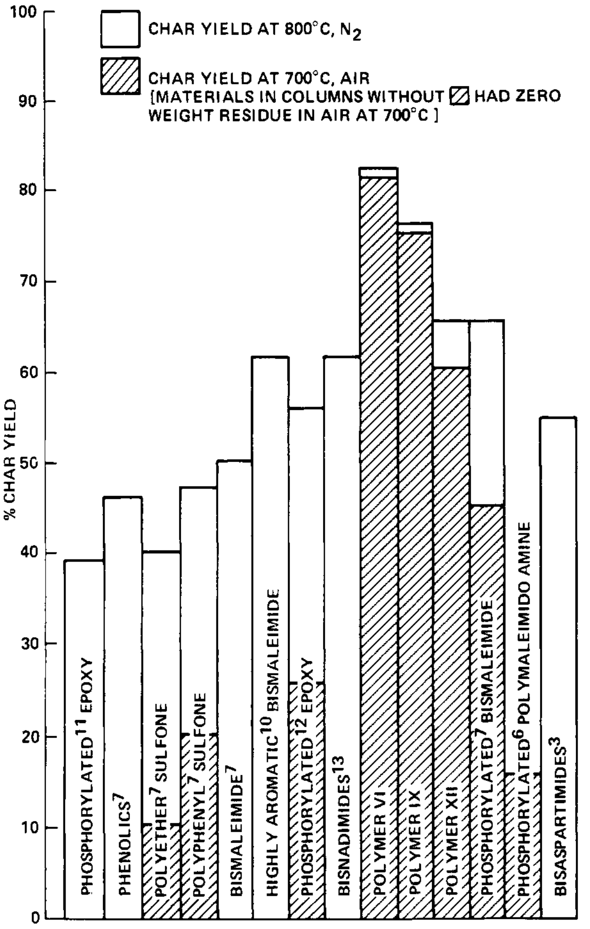


Figure 5. Comparison of char yields of polymers VI, IX, and XII with those other similar types of polymers.

obtained from polymers IX and XII. Polymers VI and IX did not burn or melt when exposed to flame, indicating their virtually incombustible nature. Figure 5 shows comparative char yields in air and nitrogen with other similar known polymers. From these results it is apparent that VI is superior in fire and heat resistance among the compared polymers.

The observation of higher char yields may be explained due to the presence of unique combination and percentages of phosphorus, nitrogen, and carbonyls in these polymers such that the thermooxidative decomposition is reduced. Minor weight loss observed in air for polymer XII near 530 °C may be due to the presence of fluorine in the chain. These polymers on heating to 800 °C showed a metallic type of luster.

Isothermal TGAs of polymer VI were performed (Figure 6) in both air and nitrogen atmospheres at 260, 350, 450, 550, and 700 °C. On heating at 350 °C in nitrogen for 24 h, only a 0.9% weight loss was observed; at 450 °C, the weight loss was 8.5%; and at 550 °C, 37%. The loss in nitrogen appeared to be linear with time. In air, the weight loss after 24 h at 260 °C was 2.5% whereas at 350 °C, it was 28%; at 395 °C the loss was 41.5% after 12 h. After 72 hours in air at 260 °C, the weight loss was about 4%. The thermooxidative decomposition in air apparently follows an exponential curve.

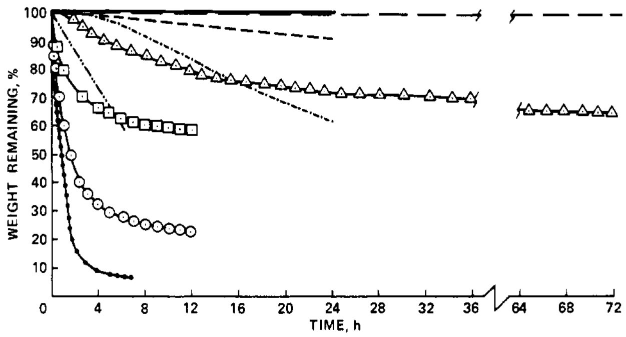


Figure 6. Isothermal gravimetric analysis of VI at a gas flow rate of 100 mL/min: (---) at 260 °C in air; (—) at 350 °C in N_2; (- - -) at 450 °C in N_2; (-··) at 550 °C in N_2; (-··) at 700 °C in N_2; (△) at 350 °C in air; (□) at 395 °C in air; (○) at 450 °C in air; (•) at 550 °C in air.

Table III
Physical Properties of Graphite Cloth Laminates Based on Polymer VI

property tested	test method	value
resin content	hydrazine method	22%
density, g/cm^3		1.47
LOI	ASTM D2863	100%
(room temperature)		100%
(300 °C)		
tensile strength	ASTM D638	58 014 psi 400 MN/m^2
elongation at break		2.65%
tensile modulus	ASTM D638	4.7 × 10^6 psi 32 407 MN/m^2
flexural strength	ASTM D790	50 347 psi 347 MN/m^2
flexural modulus	ASTM D790	7.33 × 10^6 psi 50 547 MN/m^2
short beam shear	ASTM D2344	4247 psi 29.3 MN/m^2

Composite Fabrication. Test laminates were prepared by coating graphite cloth (eight-harness satin weave cloth, designed as style 133 fabric) with a dimethylacetamide solution of cyclotriphosphazene maleimide V and drying the prepregs in an air oven at 105–110 °C for 10 min. The prepregs (four or nine plies) were stacked in a vacuum bag and pressed between aluminum plates in a heated press maintained at 160–162 °C for 20 min, 232 °C for 1.5 h, and 290 °C for 0.5 h. The pressure during curing was maintained at about 50–70 psi.

The resin contents of the laminates were determined by boiling with hydrazine hydrate. The limiting oxygen index tests (LOI) were performed both at room temperature and at 300 °C (Table III). The laminates did not burn in pure oxygen, even when heated to 300 °C prior to attempting to ignite them by flame, indicating the outstanding flame resistance of polymer VI.

Dynamic mechanical analysis (DMA) determinations were performed on four-ply laminates obtained from resin V. The glass transition temperature (T_g) of the cured sample was found to be 385 °C.

The density, shear, tensile, and flexural strength of a nine-ply laminate were determined, and the values are shown in Table III. These results indicate that the laminates from resin V can be used for structural applications.

Structure of Polymers. The outstanding properties shown by polymer VI, obtained by the thermal curing of cyclotriphosphazene maleimide V, have caused us to become interested in its structure.

It was difficult to obtain transparent KBr pellets. Therefore, the curing reaction was monitored on a NaCl disk using FT IR. The infrared spectrum of the polymer obtained after curing at 232–233 °C for 1.5 h displayed a new peak at 1642 cm^{-1}. This pattern, however, remained after the polymer was further heated to 290 °C for 0.5 h, but with an intensification of the 1642-cm^{-1} band together with broadening of the spectrum. ^{1}H NMR or ^{13}C NMR spectra of cured polymer VI in solution could not be recorded because of the polymer's insolubility even in aprotic solvents. A ^{31}P NMR spectrum of the cured sample was recorded by using magic angle spinning and cross polarization techniques. Observation of a ^{31}P NMR singlet indicates that the structure of polymer is nearly symmetrical with respect to phosphorus such that all the phosphorus remains magnetically equivalent. The position of this singlet at 8.58 ppm along with P–N stretching bands in the IR spectrum (1198, 1177, and 1164 cm^{-1}) of VI confirms the fact that the cyclotriphosphazene ring is preserved. The elemental analysis of polymer VI was the same as that of its precursor (V) (Table I), indicating that the curing reaction involves principally addition reactions. The preponderant and most probable curing reactions are the ones involving the addition of the amine to the maleimido olefinic group[16,17] (Michael-type reaction) and the homogeneous addition reactions of the maleimido olefinic bonds.[14,15,18] This accounts for the presence of the imido carbonyl peaks (1777 and 1716 cm^{-1}) in the polymer VI. A complete structure for the latter could not be deduced based on these observations.

Polymers IX, XII, and XV also are shown to have a cross-linking similar to that in the cured bismaleimides.

Degradation Behavior of Polymer VI. To gain insight regarding the degradation of polymer VI, it was heated at 800 °C under vacuum for 1 h. The residue, volatile gases, and solids collected during this thermal treatment were analyzed by IR, GC–mass spectrometry, and ^{31}P magic angle spinning NMR.

The major fragments in the mass spectra and the bands in the infrared spectra for the pyrolysis products—gases, solids, and residue—are given in Table IV. The phosphorus is retained in the char residue, most likely as the cyclotriphosphazene[19] ring (^{31}P NMR, −35 ppm).

Experimental Section

Reagents and Solvents. Hexachlorocyclotriphosphazene (I) was purified from a trimer–tetramer mixture (Aldrich Chemical Co.) after fractional vacuum sublimations at 110–120 °C (1 mm) and repeated crystallizatons from *n*-heptane (mp 110–112 °C). 4-Nitrophenol (Eastman Kodak Co.) was purified by crystallization from alcohol. Xylene was dried by refluxing with an distillation from calcium hydride. PtO_2 (Matheson Coleman and Bell) was used as received. Aniline was boiled at reflux and distilled from zinc dust. *o*-Dichlorobenzene (Eastman Kodak) was distilled. Tetrafluorosuccinic anhydride (PCR Research Chemicals, Inc.) was distilled from phosphorus pentoxide. Maleic anhydride (Eastman Kodak) was purified by crystallization with chloroform. *N,N'*-Dimethylacetamide (DMAC) (Aldrich Chemical Co.) was fractionally distilled from phosphorus pentoxide. Heptafluorobutyric anhydride (PCR Research Chemicals, Inc.) was used as received.

Analytical Equipment. Solid-state proton-decoupled ^{31}P NMR spectra were obtained in the FT mode at 36.432 MHz with a Bruker CXP-100 spectrometer equipped with a data processing system, using a solid rotor and matched spin-locked cross polarization with magic angle spinning. Proton nuclear magnetic resonance (^1H NMR) and ^{19}F NMR spectra were recorded on a Varian EM-390 NMR spectrometer. The chemical shift (δ) is given in parts per million (ppm), with tetramethylsilane as the internal standard. Infrared (IR) spectra were recorded on a Nicolet FT IR spectrophotometer with KBr pellets or on NaCl disks. GC–mass spectra were recorded by the direct-inlet procedure at 70 eV on a Hewlett-Packard 5980A mass spectrometer attached to a 5933 data system and 2100S microprogramable system computer.

Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed on a DuPont 990 thermal analyzer system. Measurements were made at a heating rate of 10 °C/min in an atmosphere of nitrogen or air at a flow rate of 100 mL/min. Melting points were determined by using a Thomas-Hoover capillary melting point apparatus; the melting points are uncorrected. The elemental analyses were done by Huffman Laboratories, Wheatridge, CO.

The flexural properties of the composites were determined with an Instron tester following ASTM D-790, using a span depth ratio of 32:1 and a crosshead speed of 0.1 in./min; the sample was 0.5 in. wide. Tensile properties were determined according to ASTM D-2344. A span-to-depth ratio of 5:1, with a crosshead speed of 0.05 in./min and a sample width of 0.498 in., was used. The flammability tests were performed with a Stanton Redcroft flammability unit.

Hexakis(4-nitrophenoxy)cyclotriphosphazene (II). This material was made following the known method of Kober et al.[8] and had a melting point of 261–264 °C (lit. mp 264 °C). Its mass spectrum showed M^+ at m/e 963. IR (KBr) (cm^{-1}) 1589 (aromatic), 1522 and 1348 (asymmetrical and symmetrical nitro group stretching, 1203, 1182, and 1163 (cyclotriphosphazene ring P=N); ^1H NMR (Me_2SO-d_6) 8.18 and 7.30 (each d_{AB}, each 12 H, J_{AB} = 10 Hz, aromatic).

Hexakis(4-aminophenoxy)cyclotriphosphazene (III). Reduction of the nitro compound II with hydrogen in aniline solution gave this material, previously reported by Allcock et al.[9] Its mass spectrum showed M^+ at m/e 783. IR (KBr) (cm^{-1}): 3419, 3371, and 3354 (NH_2 stretching), 1624 (NH_2 bending), 1505 (aromatic), 1193, 1172, and 1161 (cyclotriphosphazene ring P=N), 957, 880, and 834 (NH wagging); ^1H NMR (Me_2SO-d_6) 6.47 and 6.41 (each s, 24 H, aromatic), 4.80 (br s, 12 H, amino, exchangeable with D_2O).

Reaction of Hexakis(4-aminophenoxy)cyclotriphosphazene (III) with Maleic Anhydride: Triamino Tris(maleamic Acid) IV. To a stirred solution of hexakis(4-aminophenoxy)cyclotriphosphazene (III) (2.5 g, 0.0032 mol, in dry DMAC 12 mL), granular maleic anhydride (1.05 g, 0.0107 mol) was added in a nitrogen atmosphere. The yellow solution obtained was stirred for 8–10 h and then poured over crushed ice. The light yellow solid obtained was filtered, washed with water, and dried to yield the required amic acid IV (3.2 g): no sharp melting point; shrinking at about 300 °C.

Triamino Trismaleimide V. A solution of the triamino tris(maleamic acid) IV in DMAC was heated with stirring in a nitrogen atmosphere at 160–165 °C for 0.75–1.0 h to yield the corresponding maleimide (V) as a yellow solid. IR (NaCl disk) (cm^{-1}): 1780 and 1715 (imide carbonyl), 1637 and 1605 (amino and olefinic), 1505 (aromatic), 1197, 1177, and 1165 (cyclotriphosphazene ring, P=N), 957, 883, and 835 (POAr).

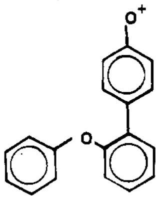
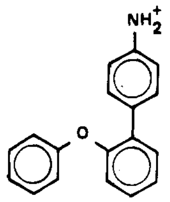
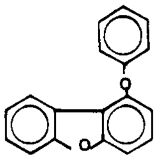
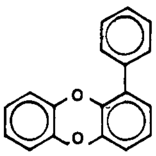
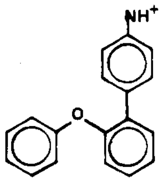
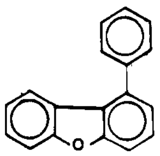
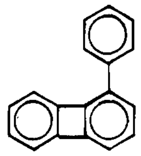
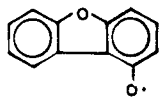
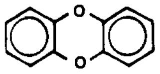
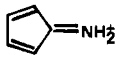
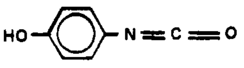
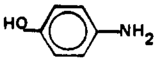
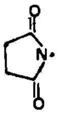
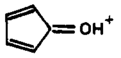
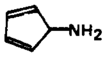
Hexakis(4-maleamidophenoxy)cyclotriphosphazene (VII). To a stirred solution of hexakis(4-aminophenoxy)cyclotriphosphazene (III) (3.91 g, 0.005 mol) in acetone (100 mL), granular maleic anhydride (2.94 g, 0.03 mol) was added at ambient temperature in a nitrogen atmosphere. A light yellow solid separated soon after the addition, and the mixture was stirred further for 2 h. The solid was filtered, washed with acetone, and dried to yield the desired maleamic acid VII (6.0 g); mp 159–160 °C. Its infrared spectrum was observed similar to that of maleamic acid IV. ^1H NMR (Me_2SO-d_6): 10.4 (s, 6 H, exchangeable with D_2O, carboxylic), 7.60 and 7.00 (each d_{AB}, J = 10 Hz, each 12 H aromatic), 6.60–6.25 (q, 12 H, J = 14 Hz, *cis*-olefinic).

Hexakis(4-maleimidophenoxy)cyclotriphosphazene (VIII). A solution of hexakis(4-maleamidophenoxy)cyclotriphosphazene (VII) in DMAC was stirred under a nitrogen atmosphere and heated to reflux (170–180 °C) for 2.5 h. The solution was cooled and poured over ice to give the desired hexakismaleimide VIII as a yellow solid. IR (KBr) (cm^{-1}): 1779 and 1716 (imide carbonyl), 1637 and 1608 (olefinic), 1543 and 1500 (aromatic), 1198, 1178, and 1165 (cyclotriphosphazene ring), 961, 947, and 839.

Reaction of Hexakis(4-aminophenoxy)cyclotriphosphazene (III) with Tetrafluorosuccinic Anhydride and Maleic Anhydride to Maleimide XI. To a three-necked flask (10 mL) equipped with a magnetic stirrer, nitrogen purge, condenser, and drying tube, a solution of hexakis(4-aminophenoxy)cyclotriphosphazene (III) (0.3 g, 0.00038 mol) in DMAC (5 mL) was added and continuously stirred. Tetrafluoroscuccinic anhydride (0.137 mL, 0.00128 mol) was injected into the DMAC solution with a syringe, and soon after, granular maleic anhydride (0.1261 g, 0.00128 mol) was added. The light yellow solution was stirred for 0.5 h in a nitrogen atmosphere to give the desired maleamic acid X. ^1H NMR (DMAC): 11.05 (s, 6 H, exchangeable

Table IV

Pyrolysis Products of Polymer VI

analyzed phase	IR, cm^{-1}	mass spectrum m/e	probable products
gases[a]	2370	44	CO_2
	2170	28	CO
	9708	17	NH_3
	930		
	1310	16	CH_4
	710	27	HCN (very small)
brown solid (eluted below 300 °C)	1600 1500 1476 1469 1254 1238 1215 1140	261	 or 
		260	 or  or 
		244	
		228	
		184	 or 
		80	
		52	
light grey solid (eluted above 300 °C)	1500 1405 1155 1148 1133 1081 1069	135	
		109	
		98	
		81	 or 

	^{31}P magic angle spinning NMR[b]	elemental analysis % C	% H	% N	% P	C/P	H/P	N/P
residue	−35.92	64.5	1.04	9.08	10.28	6.274	0.101	0.880
polymer VI	+8.58					6.245	0.432	1.341

[a] All the volatile products could not be identified. [b] Using 85% H_3PO_4 as a reference.

with D_2O, carboxylic), 10.70 (s, 6 H, exchangeable with D_2O, amido), 7.73–7.45 and 7.10–6.90 (each m, each 12 H, aromatic), 6.65–6.20 (q, 6 H, J = 14 Hz, *cis*-olefinic).

The continuously stirred solution of maleamic acid X was heated in an oil bath maintained at 150–160 °C for 1.5 h and then at 170–180 °C for 1.5 h in the presence of a nitrogen atmosphere. The reaction mixture was allowed to cool and then poured over crushed ice. The light gray solid obtained on maceration was filtered, washed with water, and dried to give the maleimide XI (0.35 g); mp 152–155 °C. IR (KBr) (cm^{-1}): 1775 and 1716 (imide carbonyl), 1614 (olefinic), 1506 (aromatic), 1200, 1178, and 1166 (cyclotriphosphazene ring, P═N and fluoro), 962, 948, and 840; ^{1}H NMR (Me$_2$SO-d_6): 7.60–7.50 (dd, J = 10 Hz and 3 Hz), 7.30–6.80 (m) (24 H, aromatic), 7.12 (s, 6 H, olefinic).

Polymerization of Maleimide XI to Polymer XII. Maleimide XI was heated in an air oven preheated to 160–162 °C; it melts and resolidifies. Heating at this temperature was continued for 0.5 h. The curing temperature was raised to 225 °C for 2 h and 300 °C for 1 h to give brown polymer XII.

Reaction of Hexakis(4-aminophenoxy)cyclotriphosphazene (III) with Heptafluorobutyric Anhydride and Maleic Anhydride To Give Maleimide XIV. Following a similar method, maleamic acid XIII was obtained by the reaction of heptafluorobutyric anhydride (0.264 mL) and maleic anhydride (0.105 g). ^{1}H NMR (DMAC): 11.35 and 10.80 (each s, 6 H and 3 H, exchangeable with D$_2$O, carboxylic and amido), 7.75–7.50 and 7.10–6.90 (each m, 24 H, aromatic), 6.70–6.20 (q, 6 H, J = 14 Hz, *cis*-olefinic).

The solution of maleamic acid XIII was heated at 160–165 °C for 0.5 h to yield the required maleimide XIV (0.35 g). IR (KBr) (cm^{-1}): 1779 and 1706 (imide carbonyl), 1637 and 1614 (olefinic), 1505 (aromatic), 1224, 1180, and 1124 (cyclotriphosphazene ring P═N and fluoro), 969, 953, 882, and 834 (POAr).

Thermal polymerization of maleimide XIV gave polymer XV using the conditions of curing given previously.

Conclusion

A novel class of fire- and heat-resistant polymers based on maleimido-substituted cyclotriphosphazenes has been synthesized. The high char yield (82% at 800 °C in N$_2$ and 81% at 700 °C in air) of polymer VI and 100% limiting oxygen index at 300 °C of its graphite laminates have demonstrated that resin V is a potential candidate for fire- and heat-resistant applications with more safety than many presently utilized resins.

Acknowledgment. We thank Dr. C. A. Fyfe, Department of Chemistry, University of Guelph, Guelph, Ontario, Canada, for providing the facility for recording the ^{31}P magic angle spinning NMR of the solid polymers.

Registry No. II, 14711-91-2; III, 13441-26-4; IV, 86118-80-1; V, 86118-78-7; polymer VI, 86118-79-8; VII, 86118-81-2; VIII, 86118-72-1; IX, 86118-73-2; X, 86128-93-0; XII, 86118-74-3; polymer XII, 86118-75-4; XIII, 86118-82-3; XIV, 86118-76-5; polymer XV, 86118-77-6; heptafluorobutyric anhydride, 336-59-4; maleic anhydride, 108-31-6; tetrafluorosuccinic anhydride, 699-30-9.

References and Notes

(1) Allcock, H. R. *Chem. Eng. News* Apr 22, 1968, pp 68–81.
(2) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Sci.* **1973**, *15*, 321.
(3) Kumar, D.; Fohlen, G. M.; Parker, J. A. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(4) Kourtides, D. A.; Parker, J. A.; Gilwee, W. J.; Lerner, N. R.; Hilado, C. J.; Labossiere, L. A.; Hsu, Ming-ta, *Sci. Tech. Aerospace Rep.* **1976**, *14-16*, Abstract N76-25354.
(5) Haiduc, I. "The Chemistry of Inorganic Systems, Part II"; Wiley-Interscience: New York, 1970; p 673 and references cited therein.
(6) Kondo, H.; Sato, M.; Yokoyama, M. *Eur. Polym. J.* **1980**, *16*, 537–541. See also their other papers on similar topics.
(7) Varma, I. K.; Fohlen, G. M.; Parker, J. A. U.S. Pat. 4 276 344 June 30, 1981.
(8) Kober, E.; Lederle, H.; Ottmann, G. *Inorg. Chem.* **1966**, *5*, 2239.
(9) Allcock, H. R.; Austin, P. E.; Rakowsky, T. F. *Macromolecules* **1981**, *14*, 1624.
(10) Varma, I. K.; Fohlen, G. M.; Parker, J. A. *J. Polym. Sci., Polym. Chem. Ed.* **1981**, *19*, 293.
(11) Kourtides, D. A.; Parker, J. A. Proceedings of the Adhesives for Industry Conference, El Segundo, CA, June 24–25, 1980.
(12) Kumar, D.; Fohlen, G. M.; Parker, J. A., unpublished work. The epoxy DEN-438 was cured with hexakis(4-aminophenoxy)cyclotriphosphazene, utilizing two of the available six amino groups.
(13) Kumar, D.; Fohlen, G. M.; Parker, J. A. *J. Polym. Sci., Polym. Chem. Ed.*, in press.
(14) Grundschober, F.; Sambeth, J. U.S. Pat. 3 380 964 (1968) and 3 533 996 (1970); Fr. Pat. 1 455 514; Neth. Appl. 6 514 767; *Chem. Abstr.* **1966**, *65*, 10746*d*.
(15) Kwiatkowski, G. T.; Robeson, L. M.; Brode, G. L.; Bedwin, A. W. *J. Polym. Sci., Polym. Chem. Ed.* **1975**, *13*, 961.
(16) Bargain, M.; Combat, A.; Grosjean, P. U.S. Pat. 3 562 223 (1971); *Chem. Abstr.* **1970**, *72*, 4047.
(17) Mallet, M. A. J.; Darmory, P. *Org. Coat. Plast.* **1974**, *34* (1), 173.
(18) Cassidy, P. E. "Thermally Stable Polymers"; Marcel Dekker: New York, 1980.
(19) Allcock, H. R. "Phosphorus-Nitrogen Compounds"; Academic Press: New York, 1972; pp 76–77.