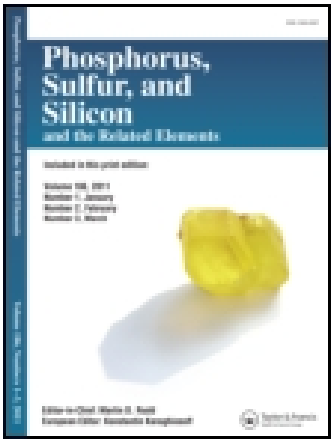

Phosphorus, Sulfur, and Silicon and the Related Elements

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Preparation and Properties of Novel Cyclophosphazenes Containing Cyanato Groups

Yuji Tada [a], Narimasa Moriya [a], Takashi Inoue [a], Atsuko Suzuki [a] & Shigeto Koyama [a]

[a] Research and Development Department, Fushimi Pharmaceutical Co., Ltd., Marugame, Japan

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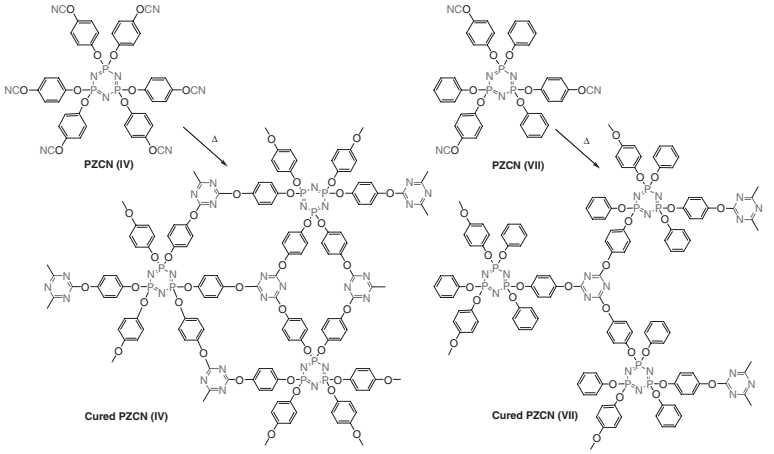
PREPARATION AND PROPERTIES OF NOVEL CYCLOPHOSPHAZENES CONTAINING CYANATO GROUPS

Yuji Tada, Narimasa Moriya, Takashi Inoue, Atsuko Suzuki, and Shigeto Koyama

Research and Development Department, Fushimi Pharmaceutical Co., Ltd., Marugame, Japan

GRAPHICAL ABSTRACT



Abstract *Novel cyclotriphosphazenes containing cyanato group (PZCN) derivatives were synthesized by a substitution reaction of 4-hydroxyphenoxycyclotriphosphazenes and cyanogen bromide (BrCN) in the presence of triethylamine (TEA). The PZCNs were characterized by FT-IR, liquid chromatography–mass spectrometry (LC-MS), ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. Curing reactions of the PZCNs were evaluated by FT-IR spectroscopy, thermogravimetry/differential thermal analysis (TG/DTA), and differential scanning, calorimetry (DSC). The PZCNs exhibited an exothermic peak due to curing within the temperature range of 140–300°C by DSC. The PZCNs were completely cured at 220°C. The cured PZCNs exhibited high thermal stability up to 350°C, a high char-forming capability, and electrical properties, such as dielectric constants (Dks) between 2.68 and 2.87, and dissipation factors (Dfs) between 0.008 and 0.013 at 1 MHz.*

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Address correspondence to Yuji Tada, Research and Development Department, Fushimi Pharmaceutical Co., Ltd., Marugame, Japan. E-mail: ytada@fushimi.co.jp

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Keywords Cyclophosphazenes; cyanates; dielectric properties; thermal properties

INTRODUCTION

Cyanate resins (CRs) are a category of thermoset resins in which cyanate ester monomers polymerize by a cyclotrimerization reaction to a cyanurate (often referred to as an *s*-triazine)-linked network polymer. The CRs have attracted commercial and scientific interest due to their thermal, mechanical, and processing properties, especially their dielectric properties, such as the dielectric constant (Dk) and the dissipation factor (Df). The CRs have been applied to products ranging from composites for aerospace to insulating materials for electronics.[1–6]

In particular, CR applications in reinforced circuit boards and in the thin-film insulation of high-density interconnect devices, termed multi-chip modules (MCMs), are driven by the benefits of faster operating speeds, smaller sizes, reduced crosstalk, reduced power requirements, and reduced heat production (inversely related to the square root of the Dk). Lower Dfs are known to proportionally reduce power loss and heat production.[1]

Phosphazenes have been investigated as forms of cyclic monomers or linear polymers over wide ranges. Many phosphazene derivatives with reactive functional groups (e.g., amino, hydroxyl, glycidyl, isocyanato, vinyl, etc.) or without reactive functional groups have been prepared and evaluated in the literature.[7–9] It is well known that phenoxyphosphazenes, without reactive functional groups, exhibit high resistances to hydrolysis, high thermal stability, and high flame retardancy as an alternative halogen-free flame retardant.[10,11] Phenoxyphosphazene derivatives are proposed as candidates for applications as additives, coatings, adhesives, composites, and electronic materials.

Mathew et al.[12] reported hydroxyphenyl-substituted cyclotriphosphazenes prepared from hexachlorocyclotriphosphazene with phenol and bisphenol-A. These cyclotriphosphazenes were converted to their corresponding cyanate-functional compounds for applications in stringent fire resistance norms, such as in aircraft interiors and in the transportation industry. However, the phenol-functionalized cyclotriphosphazenes possess multiply linked structures because bisphenol-A, having bi-functionality, was directly reacted to hexachlorocyclotriphosphazene. The cyanato-density of the resulting cyanato-functionalized cyclotriphosphazenes is lower than that of the compound without the structure multiply linked with bisphenol-A. The flame retardancy and the char-yielding properties of the polymer improved with increased crosslinking, the Dk and Df performance of the polymer constructed simply with phosphazene and triazine rings, however, was not obtained with the multiply linked structure that resulted from the reaction method.

In this paper, we have synthesized novel cyclophosphazenes with cyanato groups that do not have a cross-linked structure. The synthesis was achieved by the reaction of a cyclophosphazene containing a hydroxyphenoxy group with cyanogen bromide (BrCN) and triethylamine (TEA), and the thermal and electrical properties of the phosphazenes were evaluated.

RESULTS AND DISCUSSION

Synthesis and Characterization

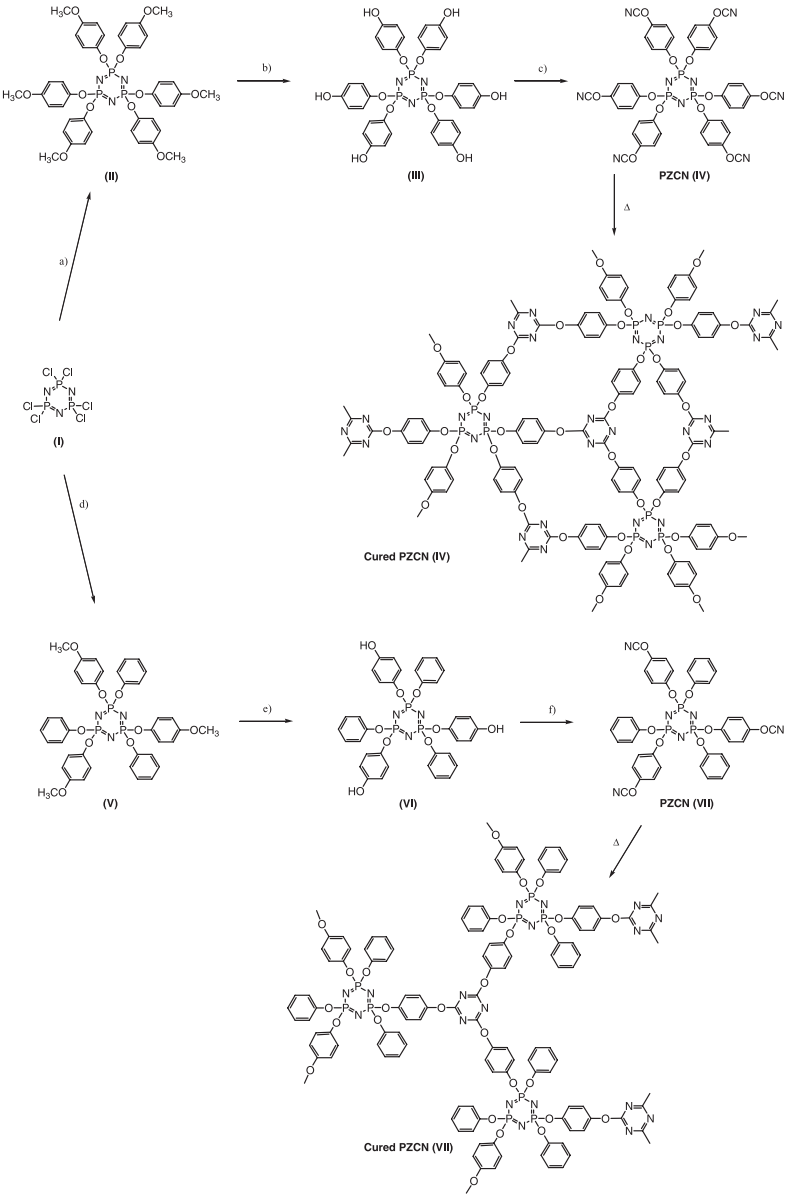
Cyclophosphazenes containing cyanato groups (PZCN, **IV** and **VII**) were synthesized by the reaction of 4-hydroxyphenoxycyclotriphosphazenes (**III** and **VI**) with BrCN in the presence of a base. The phosphazenes (**III**) and (**VI**) were prepared from hexachlorocyclotriphosphazene (**I**) via 4-methoxyphenoxycyclophosphazenes (**II**) or (**V**) as shown in Scheme 1, according to methods reported in the literature.[13–15]

The 4-methoxyphenoxyphosphazenes (**II**) or (**V**) were first prepared by substitution of (**I**) with an alkaline metal salt of 4-methoxyphenol or a mixture of 4-methoxyphenol and phenol in yields of 87.3–96.4%. Subsequently, the methyl group of (**II**) and (**V**) was deprotected by pyridine-hydrochloride (instead of BBr_3 as reported by Medici et al.[15]) to give 4-hydroxyphenoxyphosphazenes (**III**) and (**VI**) in yields of 98.7% and 88.9%, respectively. The tris(4-hydroxyphenoxy)tris(phenoxy)cyclotriphosphazene (**VI**) has been confirmed to be substituted with phenoxy and 4-hydroxyphenoxy in the position of germinal and nongeminal, mainly nongeminal, by the ^{31}P NMR spectroscopy.

The PZCNs (**IV**) or (**VII**) were prepared by reaction of the corresponding 4-hydroxyphenoxyphosphazenes (**III**) or (**VI**) and BrCN in the presence of TEA under moisture-free conditions. The cyanation reaction with BrCN and TEA gave rise to diethylcyanamide as a side product. However, the diethylcyanamide and other impurities were completely eliminated from the PZCNs by recrystallization or reprecipitation with the confirmation of gas chromatography (GC) and ^1H NMR such that trace impurities did not affect the curing reaction with the cyanato group of the PZCNs. The resulting PZCNs (**IV**) and (**VII**) were obtained in yields of 90.8% and 72.5%, respectively, and were characterized by the ^{13}C and ^{31}P NMR, FT-IR, and liquid chromatography–mass spectrometry (LC-MS).

The formation of PZCN (**IV**) from 4-hydroxyphenoxyphosphazene (**III**) can be observed characteristically by the IR spectroscopy. Absorption based on the hydroxy group disappeared at 3292 cm^{-1} for (**III**), and the characteristic absorption of the cyanato group appeared at 2272 and 2237 cm^{-1} for (**IV**), which was split into partially resolved bands. Five signals were observed in the ^{13}C NMR spectrum for PZCN (**IV**) as shown in Figure 1, of which four signals at 117.8, 123.6, 149.1, and 150.9 ppm were based on the carbon of the phenylene group and one signal, at 109.2 ppm, was based on the carbon of the cyanato group, as supported by the work of Fyfe et al.[16] Further, the structure of PZCN (**IV**) was elucidated to be substituted with six of the 4-cyanatophenoxy groups on the phosphazene ring by LC-MS analysis. The cyanato equivalent weight of PZCN (**IV**) was calculated to be 157 g/eq based on this analysis.

The formation of PZCN (**VII**) from 4-hydroxyphenoxyphosphazene (**VI**) was also confirmed by the IR spectroscopy. Absorption based on the hydroxy bond disappeared at 3325 cm^{-1} for (**VI**), and an alternative new absorption based on the cyanato bond appeared at 2270 and 2236 cm^{-1} with resolved bands for (**VII**). Nine signals were observed in the ^{13}C NMR spectrum of PZCN (**VII**) as shown in Figure 2, with eight signals at 117.5, 121.6, 123.6, 126.3, 130.6, 149.4, 150.5, and 151.1 ppm attributed to the carbon of the phenyl and phenylene groups, and one signal at 109.3 ppm attributed to the carbon of the cyanato group. The PZCN (**VII**) is determined to be a mixture of $N_3P_3(OC_6H_4OCN)_2(OC_6H_5)_4$, $N_3P_3(OC_6H_4OCN)_3(OC_6H_5)_3$, and $N_3P_3(OC_6H_4OCN)_4(OC_6H_5)_2$ whose protonated molecule ions were observed at *m/z*



a) $MeOC_6H_4ONa$ in toluene and THF, b) PyHCl at 200°C for 3 h, c) BrCN, Et_3N, acetonitrile d) PhONa, $MeOC_6H_4ONa$ in toluene and THF, e) PyHCl at 200°C for 3 h, f) BrCN, Et_3N, MIBK.

Scheme 1

776, 817, and 858, respectively, by LC-MS. Furthermore, the PZCN (**VII**) is estimated to have a mean structure of $N_3P_3(OC_6H_4OCN)_3(OC_6H_5)_3$ by the ^1H NMR spectroscopy, and the cyanato equivalent weight of the PZCN (**VII**) was calculated to be 272 g/eq based on this analysis. As a result, the PZCNs (**IV**) and (**VII**) were confirmed to possess

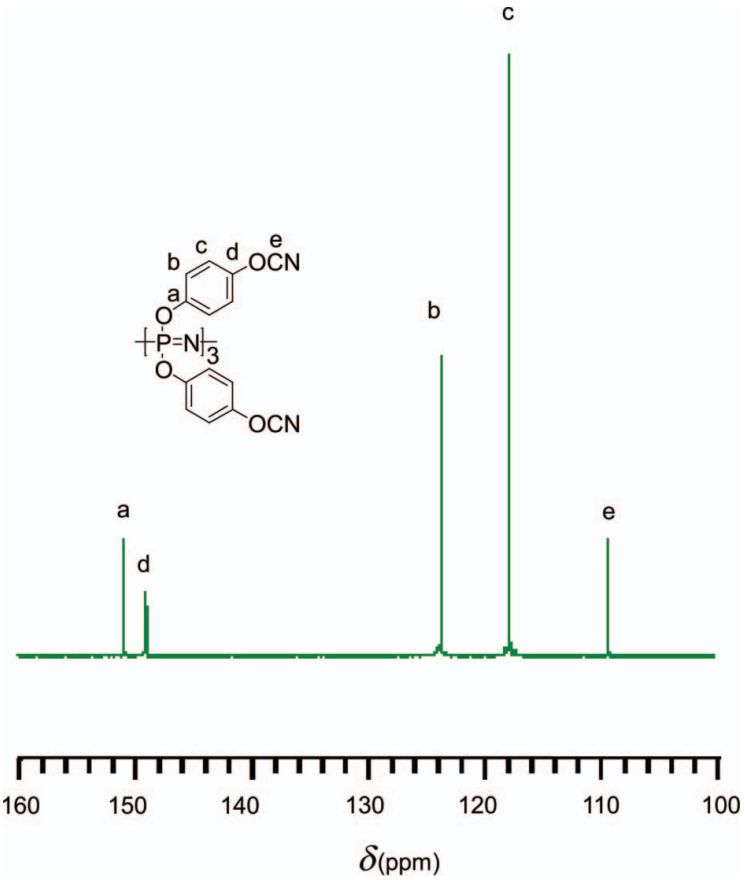


Figure 1 ^{13}C NMR of spectrum of PZCN (**IV**).

cyanato groups on molecules that are able to form triazine rings with trimerization by heating.

In addition, ionic impurities in the PZCNs (**IV**) and (**VII**) were detected at concentrations less than 10 ppm by IEC; therefore, the prepared PZCNs (**IV**) and (**VII**) were determined to be suitable for the evaluation of their electrical properties.

Curing Study

The thermal aspects of the PZCNs (**IV**) and (**VII**) were investigated by differential scanning calorimetry (DSC). PZCN (**IV**) exhibited a sharp endothermic peak due to its melting point at 150°C, followed by a broad exothermic peak due to the curing reaction in the temperature range of 160–280°C, with a maximum at 233°C in the thermogram. PZCN (**VII**) exhibited only a broad exothermic peak due to the curing reaction in the temperature range of 140–300°C, with a peak at 255°C. Because PZCN (**VII**) consists of a mixture of substituted di-, tri-, and tetra-cyanatophenoxy groups, including stero and regio isomers substituted in geminal and nongeminal positions, resulting in PZCN (**VII**) having a viscous oily nature.

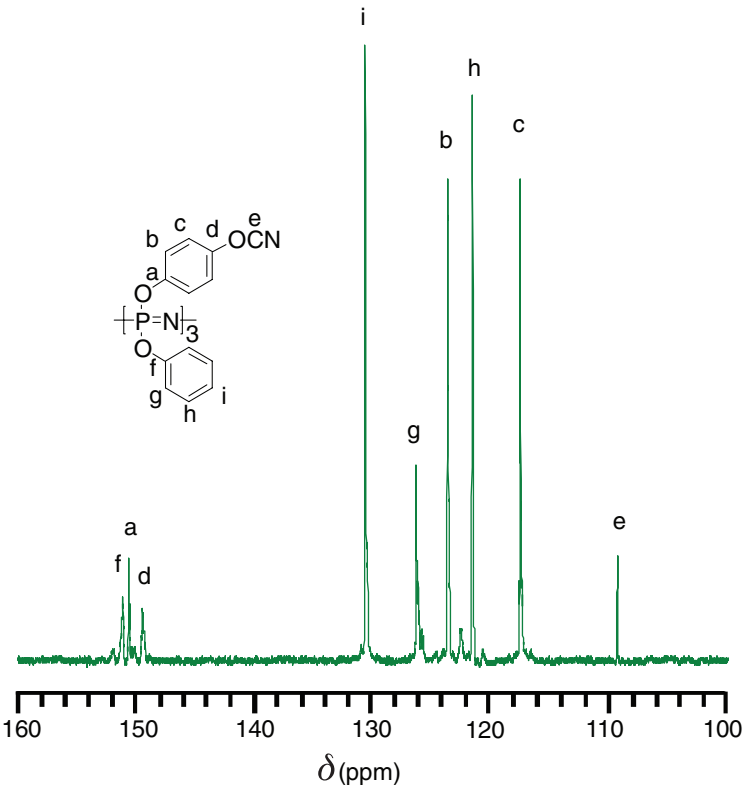


Figure 2 ^{13}C NMR spectrum of PZCN (**VII**) (Color figure available online).

After the PZCNs (**IV**) and (**VII**) were heated to 280°C and 300°C, respectively, the samples were cooled to room temperature in a nitrogen atmosphere. The structure of the samples was determined using the IR spectroscopy, and their spectra compared with starting samples are shown in Figure 3. The IR spectra of the PZCNs (**IV**) and (**VII**) showed absorptions based on the phosphazene rings and the phenoxy groups at 1593, 1495, 1169, and 954 cm^{-1}. Additionally, the characteristic absorptions of the C–N triple bond showed up at both 2270–2272 cm^{-1} and 2235–2237 cm^{-1}. After the PZCNs (**IV**) and (**VII**) were heated up to 280°C and 300°C, respectively, the absorptions based on the C–N triple bond disappeared completely, and the characteristic absorptions based on the triazine rings appeared at 1570 cm^{-1} for N—C=N and at 1374 cm^{-1} for N–C–O. Hence, the cyanate group of the PZCNs (**IV**) or (**VII**) cyclotrimerized exothermically to form triazine ring structures, resulting in a tightly cross-linked structure as shown in Scheme 1.

Thermal Properties of PZCNs

The properties of the cured PZCNs (**IV**) and (**VII**) were evaluated after precuring treatments at 140°C for 2 h and 2 h, respectively, and following postcuring at 220°C for 14 h and 3 h, respectively. After the PZCNs (**IV**) and (**VII**) were postcured, the PZCNs turned from tacky liquids to dimensionally stable solids. At the same time, the conformational

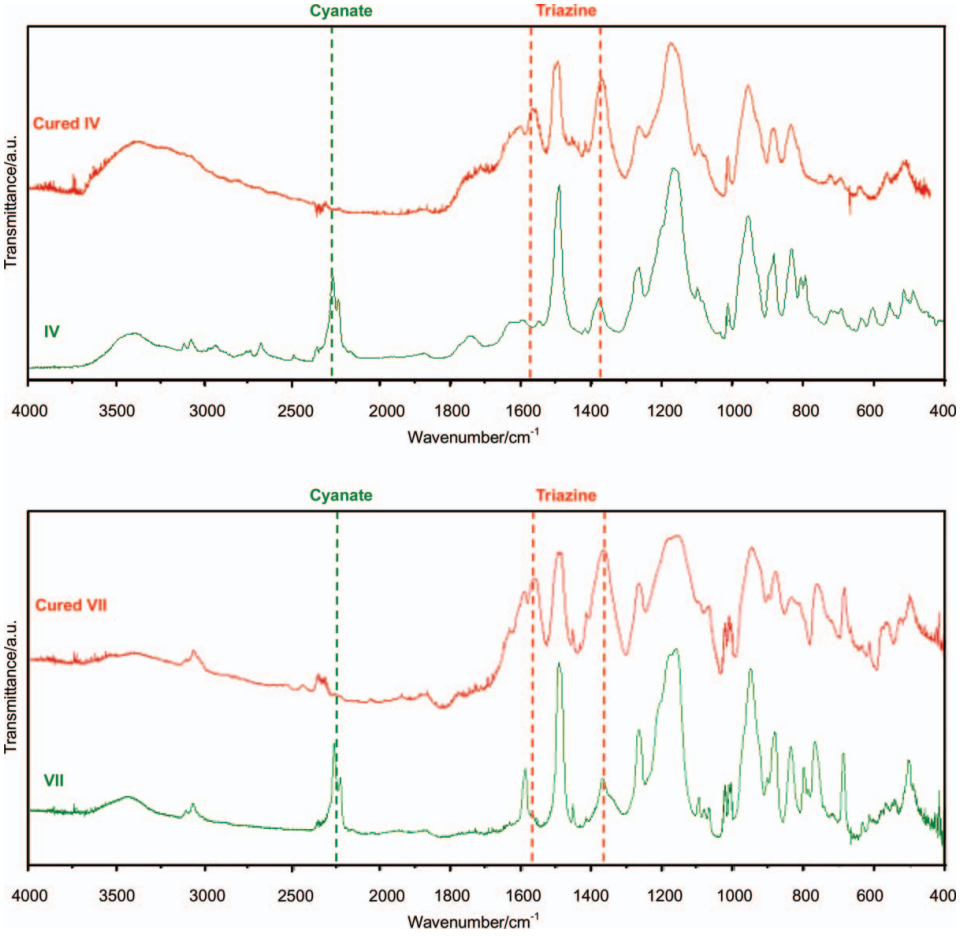


Figure 3 IR spectra of PZCNs and cured PZCNs (Color figure available online).

transition from the cyanates to the triazines was confirmed by the IR spectroscopy as shown in Figure 3.

Figure 4 shows thermogravimetry curves of the cured PZCNs (**IV**) and (**VII**) taken in a nitrogen atmosphere. The results are summarized in Table 1. The cured PZCNs (**IV**) and (**VII**) were stable up to 350°C without weight loss. The 5% weight loss temperature of the

Table 1 Thermal and electrical properties of cured PZCN (**IV**), (**VII**), and BPACN

Cured	Td5% (°C)	Td10% (°C)	Residue at 600°C (%)	Dielectric constant (Dk)	Dissipation factor (Df)
PZCN (**IV**)	424	461	75.0	2.87	0.013
PZCN (**VII**)	436	467	71.0	2.68	0.008
BPACN	425	438	47.5	2.91[a]	0.005[a]

[a]Dk: 2.91, Df: 0.005 in literature.

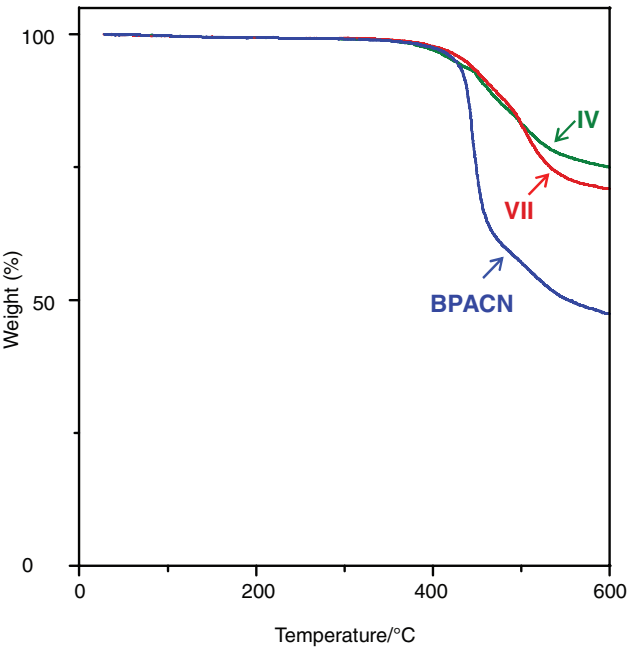


Figure 4 TG analysis of cured PZCNs (**IV**), (**VII**), and BPACN (Color figure available online).

cured PZCNs (**IV**) and (**VII**) was determined to be 424°C and 436°C, respectively. Moreover, the cured PZCNs (**IV**) and (**VII**) had high char residues, including 75.0% and 71.0% at 600°C, respectively. The cured PZCNs (**IV**) and (**VII**) were compared with 2,2-bis(4-cyanatophenyl)propane (BPACN) that was a commercially available simple cyanate compound. Although, the cured PZCNs (**IV**) and (**VII**) showed initial weight loss temperatures similar to the cured BPACN, the cured PZCNs (**IV**) and (**VII**) exhibited characteristically larger char residues than the cured BPACN at 600°C.

The cyanate-functionalized cyclotriphosphazenes consisting of cyclotriphosphazene, phenol, and bisphenol-A reported in the literature had weight losses beginning at 200°C and had ca. 50% char residue at 600°C.[12] The PZCN (**IV**) substituted with six cyanatophenoxy groups showed a particularly high char residue at 600°C. The PZCNs (**IV**) and (**VII**) were of high purity with high phosphazene content. While the reported cyclotriphosphazenes included cross-linked structures, they were difficult to purify to low impurity levels. The PZCNs (**IV**) and (**VII**) have a high phosphazene ring because the PZCNs (**IV**) and (**VII**) derive from (**IV**) and (**VII**) with six and three hydroxyphenoxy groups, respectively, instead of isopropylidene diphenoxy groups.

Electrical Properties of PZCNs

Novel phosphazenes containing cyanato groups, PZCNs (**IV**) and (**VII**), with high phosphazene content were prepared without a multiply linked structure. The Dk and Df of the cured PZCNs were measured at a 1 MHz frequency at room temperature, as summarized in Table 2. Although, the cured PZCNs (**IV**) and (**VII**) showed Dk values less than 3, similar to the cured BPACN, the Dk values of the cured PZCNs (**IV**) and (**VII**) were slightly higher than that of the cured BPACN. The phosphazene and triazine rings that consist of a plain

six-membered cyclic structure are irrelevant to both the Dk and Df values of the PZCNs. Thus, the electrical properties of the PZCNs maintain low Dk and Df values with high phosphazene and triazine rings content.

Additionally, where difunctional phenols are reacted with hexachlorocyclotriphosphazene, the resulting products include cross-linked structures that are difficult to make soluble in common solvents. Consequently, these cross-linked compounds are difficult to purify to low levels of ionic impurities based on a substitution reaction (in which the leaving group is an alkali metal halide) by using the alkali metal of the phenols with the hexachlorocyclotriphosphazene. Therefore, the phosphazenes obtained in our process are able to achieve a low ionic impurity level by purification, as needed to attain high dielectric properties.

The PZCNs may become good candidates for electric or electronic applications due to their low Dk and high flame retardancy.

Flame Retardancy of PZCNs

The flame retardancy of the cured PZCNs was evaluated by the UL-94 vertical test method. The cured PZCNs showed V–0 rating at 0.8 mm thickness, but the cured BPACN burned at the same thickness. The cured PZCNs showed excellent flame-retardancy compared with the cured BPACN. The PZCNs will be able to enhance the flame retardancy of other matrix polymers, such as epoxy and CRs.

The resulting PZCNs can be used as candidates for flame-retardant additives, as needed in the electric industry because of their low dielectric properties, in addition to their application in stringent fire resistant norms, such as in aircraft interiors and the transport industry.

CONCLUSIONS

Novel PZCN derivatives were synthesized by a substitution reaction of 4-hydroxyphenoxycyclophosphazene and BrCN with TEA in high yield. After the PZCNs were postcured at 220°C, the resulting cured PZCNs exhibited high thermal stabilities of up to 350°C, high char-forming capabilities, and electrical properties, such as dielectric constants (Dks) of 2.68–2.87 and dissipation factors (Dfs) of 0.008–0.013 at 1 MHz. Hence, the PZCN derivatives exhibited properties well suited for high-speed and high-density multi-layer boards in the microelectronics industry.

EXPERIMENTAL

Materials

Hexachlorocyclotriphosphazene (**I**) $(NPCl_2)_3$ was purified by recrystallization from hexane and dried under reduced pressure. BrCN was purchased from Sigma–Aldrich Co., Saint Louis, MO, USA, and used as received. Solvents were purified by conventional methods, and other reagents were of reagent grade and used without further purification. All reactions were carried out in a nitrogen atmosphere. Hexakis(4-hydroxyphenoxy)cyclotriphosphazene (**III**) was prepared by the reaction of $(NPCl_2)_3$ (**I**) with the sodium salt of 4-methoxyphenol to form hexakis(4-methoxyphenoxy)cyclotriphosphazene (**II**) and then by demethylating (**II**) with an excess of pyridine-hydrochloride instead of BBr_3, as reported in the literature.[13–15] The melting point

was 241–242°C experimentally and 241–243°C in the literature.[15] BPACN was purchased as PRIMASET® BADCy from LONZA Ltd., Basel, Switzerland, and used as received.

Measurements

The ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectra were recorded on a Varian Unity 300 FT-NMR spectrometer at 300 MHz, 75 MHz, and 121 MHz, respectively. Deuterated chloroform ($CDCl_3$) and deuterated acetone (acetone-d_6) were used as solvents. Tetramethylsilane (TMS) was used as an internal standard for the ^{1}H NMR and ^{13}C NMR, and 85% phosphoric acid was used as an external standard for the ^{31}P NMR. LC–MS measurements were conducted on a Thermo Finnigan LCQ Advantage MAX ion-trap mass spectrometer (ESI^+) coupled to a Surveyor HPLC system (Thermo Fisher Scientific, Inc., Waltham, MA) equipped with a C18 (Inertsil ODS-2, 4.6 mm D, 250 mm L, 5 μm particle size, GL Sciences Inc., Tokyo, Japan) analytical column and buffers A: acetonitrile and B: 0.1% aq. formic acid. Thermogravimetric analysis (TGA) and DSC were performed using a Shimadzu DTG 60 and DSC 60 analyzer (Shimadzu Corporation, Kyoto, Japan), respectively, at a heating rate of 10°C min^{-1} under a nitrogen flow of 50 mL min^{-1}. Both Dk and Df were measured at 1 MHz at room temperature using an Agilent 4284A Precision LCR Meter (Agilent Technologies, Inc., Santa Clara, CA). Additional experimental details are found in the Supplemental Materials (available online).

Synthesis of Cyclophosphazenes Containing Cyanato Groups; Synthesis of Hexakis(4-cyanatophenoxy)cyclotriphosphazene (IV)

A solution of hexakis(4-hydroxyphenoxy)cyclotriphosphazene (**III**) (450.0 g, 1.71 unit mol), BrCN (444.9 g, 4.20 mol), and acetonitrile (5750 mL) was cooled to −10°C, and TEA (425.0 g, 4.20 mol) in acetonitrile (640 mL) was added dropwise with stirring below 0°C, and then stirred at the same temperature for 30 min. Water (2500 mL) was added to the reaction mixture and stirred for 30 min. The resulting precipitate was collected and washed with water (800 mL) and toluene (570 mL) to give a wet 655 g of crude product as a pale-brownish solid. The crude product was purified by recrystallization from acetone/heptane (1:1) to give 486.0 g of hexakis(4-cyanatophenoxy)cyclotriphosphazene (**IV**) as a white solid with a yield of 90.8%.

Melting point: 150°C. ^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 7.03 (d, 2H, $J = 12.4$ Hz, H of aromatic ring), 7.15 (d, 2H, $J = 12.4$ Hz, H of aromatic ring), ^{13}C NMR (75 MHz, acetone-d_6, δ, ppm): 109.2, 117.8, 123.6 (q), 149.1 (q), 150.9, ^{31}P NMR (121 MHz, $CDCl_3$, δ, ppm): 9.2 (s, phosphorous of cyclophosphazene); IR (KBr, pellet, ν, cm^{-1}): 2272 and 2237 (s, ν_{C-N}), 1495 (vs, ν_{C-C}), 1169 (s, ν_{P-N-P}), 954 (s, ν_{P-O-C}), 883 (m, ν_{P-N-P}), 833 (m); LC-MS (positive-ESI, m/z): 941 ($M+H^+$), 963 ($M+Na^+$).Cyanato equivalent weight: $940(M^+)/6 = 157$ g/eq.

Synthesis of Tris(4-methoxyphenoxy)tris(phenoxy)cyclotriphosphazene (V)

A mixture of phenol (purity: 99%, 585.6 g, 6.16 mol), toluene (3550 mL), and 44% NaOH aq. solution (549.1 g, 241.6 g as NaOH, 6.04 mol) was heated to 110°C. The mixture was stirred while refluxing, and the water was removed from azeotropically distilled toluene–water until the water content of the mixture was less than 100 ppm. The

mixture was concentrated and dissolved in tetrahydrofuran (THF; 1560 mL). The resulting solution was added to hexachlorocyclotriphosphazene (**I**) (700.0 g, 6.04 unit mol) in toluene (11660 mL) while stirring for 8 h at 10°C or below. The reaction mixture was stirred for 1 h at the same temperature, and then warmed up to 25°C to give intermediate. The composition of the intermediate was calculated as nongeminal $P_3N_3(OC_6H_5)_3Cl_3$ 65.8%, germinal $P_3N_3(OC_6H_5)_3Cl_3$ 16.9%, $P_3N_3(OC_6H_5)_2Cl_4$:10.3%, and $P_3N_3(OC_6H_5)_4Cl_2$ 7.0% from the integrals of the ^{31}P NMR spectrum. Mean structure estimated from the ^{31}P NMR: $N_3P_3(OC_6H_5)_{3.0}Cl_{3.0}$ (see Figure S1 available online in the Supplemental Materials).

A mixture of 4-methoxyphenol (purity: 99%, 988.1 g, 7.88 mol), toluene (7600 mL), and 44% KOH aq. solution (994.5 g, 437.6 g as KOH, 7.80 mol) was heated to 110°C, and the water was removed from azeotropically distilled toluene–water until the water content of the mixture was less than 100 ppm. The reaction mixture was cooled to below 40°C, and the toluene solution of the trichlorotriphenoxycyclotriphosphazenes was added. The mixture was heated, and the THF was distilled off. After the mixture was stirred at 110°C for 12 h, the mixture was cooled to room temperature, and a 2% NaOH aq. solution (3000 mL) was added. The organic layer was washed with 5% NaOH aq. solution (3000 mL). Water (3000 mL) was then added to the organic layer, and the pH of the aqueous layer was adjusted to 3 by addition of a 4% HCl aq. solution. The organic layer was concentrated under a reduced pressure to give 1521.0 g of tris(4-methoxyphenoxy)-tris(phenoxy)cyclotriphosphazene (**V**) as a dark brown viscous liquid with a yield of 96.4%.

Mean structure estimated from the ^1H NMR: $N_3P_3(OC_6H_4OCH_3)_{3.0}(OC_6H_5)_{3.0}$.

^1H NMR (300 MHz, $CDCl_3$, δ, ppm): 3.76 (s, 3H, O*CH*$_3$), 6.8–7.3 (m, 9H, aromatic ring), ^{31}P NMR (121 MHz, $CDCl_3$, δ, ppm): 10.7 (s, phosphorus of cyclophosphazene).

Synthesis of Tris(4-hydroxyphenoxy)tris(phenoxy)cyclotriphosphazene (VI)

To a solution of pyridine (556.9 g, 7.04 mol) in toluene (1630 mL), gaseous hydrogen chloride (295.0 g, 8.09 mol) was introduced at less than 10°C. After the preparation of the pyridine-hydrochloride/toluene mixture, tris(4-methoxyphenoxy)tris(phenoxy)cyclotriphosphazene (**V**) (1413.2 g, 5.41 unit mol) was added. The mixture was heated, and the toluene was distilled off. Finally, the mixture was heated to 200–205°C and stirred for 3 h at this temperature. The reaction mixture was cooled to less than 40°C, and 4-methylpentan-2-one (MIBK, 2570 mL) and 3% HCl aq. solution (2160 mL) were added. The organic layer was washed with 3% HCl aq. solution (2170 mL). Moreover, water (1060 mL) was added to the organic layer, and the pH of the aqueous layer was adjusted to 6 by addition of 10% NaOH aq. solution. The organic layer was washed with water (2000 mL) and was concentrated under a reduced pressure to give 1189.4 g of tris(4-hydroxyphenoxy)tris(phenoxy)cyclotriphosphazene (**VI**) as a dark brown viscous liquid with a yield of 88.9%.

Mean structure estimated from the ^1H NMR: $N_3P_3(OC_6H_4OH)_{3.0}(OC_6H_5)_{3.0}$.

^1H NMR (300 MHz, acetone-d_6, δ, ppm): 6.7 (m, 4 H, H^2 and H^6 of quinone, and H^3 and H^5 of phenoxy), 6.94 (dd, 2 H, H^3 and H^5 of quinone), 7.18 (m, 1 H, H^4 of phenoxy), 7.27 (m, 2 H, H^2 and H^6 of phenoxy), 8.35 (brs, 1H, OH), ^{31}P NMR (121 MHz, acetone-d_6, δ, ppm): 10.7 (s, phosphorus of cyclophosphazene).

IR (KBr, pellet, ν, cm^{-1}): 3325 (b, ν_{O-H},), 1593 (m, ν_{C-C}), 1508 (s, ν_{C-C}), 1489 (s, ν_{C-C}), 1188 (s, ν_{P-N-P}), 1176 (s, ν_{P-O-C}), 956 (s, ν_{P-O-C}), 877 (m, ν_{P-N-P}), 835 (m);

LC-MS (positive-ESI, *m*/*z*).

$N_3P_3(OC_6H_4OH)_2(OC_6H_5)_4$: 726 $(M + H^+)$, 748 $(M + Na^+)$,

$N_3P_3(OC_6H_4OH)_3(OC_6H_5)_3$: 742 $(M + H^+)$, 764 $(M + Na^+)$,

$N_3P_3(OC_6H_4OH)_4(OC_6H_5)_2$: 758 $(M + H^+)$, 780 $(M + Na^+)$.

Synthesis of Tris(4-cyanatophenoxy)tris(phenoxy)cyclotriphosphazene (VII)

A solution of tris(4-hydroxyphenoxy)tris(phenoxy)cyclotriphosphazene (**VI**) (500.0 g, 2.02 unit mol), BrCN (251.0 g, 2.37 mol), and MIBK (1030 mL) was cooled to −10°C, and a TEA (239.8 g, 2.37 mol) in acetonitrile (1750 mL) solution was added dropwise with stirring below 0°C, followed by stirring at this temperature for 30 min. Into this reaction mixture, toluene (3500 mL) and water (1750 mL) were added and stirred for 30 min. The organic layer was washed with water (1750 mL) and concentrated under a reduced pressure below 40°C to give 638.9 g of the crude product as a brownish viscous oil. The crude product was purified by reprecipitation with toluene–heptane seven times to give 398.6 g of tris(4-cyanatophenoxy)tris(phenoxy)cyclotriphosphazene (**VII**) as a brownish viscous oil with a yield of 72.5%.

^{1}H NMR (300 MHz, $CDCl_3$, δ, ppm): 6.80–7.08 (m, 4H, aromatic ring), 7.10–7.28 (m, 5H, aromatic ring), ^{13}C NMR (75 MHz, acetone-d_6, δ, ppm): 109.3, 117.5 (q), 121.6, 123.6, 126.3, 130.6, 149.4 (q), 150.5, 151.1, ^{31}P NMR (121 MHz, $CDCl_3$, δ, ppm): 9.7 (s, phosphorous of phosphazene ring).

IR (KBr, pellet, ν, cm^{-1}): 2270 and 2235 (s, ν_{C-N}), 1591 (s, $\nu_{C=C}$), 1496 (vs, $\nu_{C=C}$), 1182 (s, ν_{P-N-P}), 1163 (s, ν_{P-O-C}), 953 (s, ν_{P-O-C}), 883 (m, ν_{P-N-P}), 840 (m).

LC-MS (positive-ESI, m/z): $N_3P_3(OC_6H_4OCN)_2(OC_6H_5)_4$: 776 $(M + H^+)$, 798 $(M + Na^+)$,

$N_3P_3(OC_6H_4OCN)_3(OC_6H_5)_3$: 817$(M + H^+)$, 839 $(M + Na^+)$,

$N_3P_3(OC_6H_4OCN)_4(OC_6H_5)_2$: 858 $(M + H^+)$, 880 $(M + Na^+)$.

Curing conditions for Hexakis(4-cyanatophenoxy)cyclotriphosphazene (IV) and Tris(4-cyanatophenoxy)tris(phenoxy)cyclotriphosphazene (VII)

The PZCN (**IV**) was dissolved at a concentration of 50% by weight in 1-methoxy-2-(2-methoxyethoxy)ethane (Diglyme) and then preheated to 140°C for 30 min. The PZCN (**VII**) was preheated at 140°C for 45 min.

The preheated PZCNs (**IV**) or (**VII**) were poured and spread on polyethylene terephthalate (PET) films that were preheated to 140°C and were then precured at 140°C for 2 h.

The resulting films were separated from the PET films and were postcured at 220°C for 14 h and 3 h, respectively, to give the films for measurement.

As a reference, after the BPACN was precured at 140°C for 40 h and postcured at 250°C for 4 h and 285°C for 2 h, the cured BPACN was evaluated.

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