# Thermally stable and flame retardant low dielectric polymers based on cyclotriphosphazenes

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We prepared thermally stable, low dielectric polymers by thermal polymerization of cyclotriphosphazenes bearing acetylene or styrene groups. Homosubstituted cyclotriphosphazene 1, containing acetylene groups, was synthesized by reaction of hexachlorocyclotriphosphazene with sodium salts of 4'-trimethylsilylethynyl-1,1'-biphenyl-4-ol and subsequent removal of trimethylsilyl groups under basic conditions. Heterosubstituted cyclotriphosphazene 2 was prepared using 4phenylphenol as a cosubstituent. Cyclotriphosphazene 3 with styrene groups was prepared by reaction of hexachlorocyclotriphosphazene with sodium salts of 4-hydroxystyrene. Highly cross-linked polymers were obtained by thermal polymerization of the cyclotriphosphazenes at 200 °C for 1 and 2 and at 150 °C for 3. The 5% weight loss temperatures of the cross-linked polymers of compounds 1-3. measured by TGA, were above 470 °C. The flame-retardant property of the polymers was evaluated by measuring LOI (limiting oxygen index) values. The polymers of cyclotriphosphazenes 1-3 showed very high LOI values of 52, 50 and 49, respectively. We also prepared copolymers of cyclotriphosphazene 3 with styrene by UV irradiation in the presence of a photoinitiator (2,2-dimethoxy-2phenylacetophenone). In the TGA thermograms, the copolymers showed good thermal stability, nearly comparable to the homopolymer of 3 when the composition of 3 was higher than 60%. The dielectric properties of the polymers were measured by a metal-insulator-metal method. The polymer obtained from acetylene-containing cyclotriphosphazene 1 showed dielectric constant and dielectric loss values of about 3.12 and 0.0016, respectively, at 1 GHz. The polymer of cyclotriphosphazene 3 showed a dielectric constant of 2.4 and a dielectric loss of 0.0014 at 1 GHz.

# Introduction

Over the past few decades, the number of components on an integrated circuit (IC) has been dramatically increased along with the continual miniaturization of the devices. As a result, the IC has now become heavily populated with transistors and connection wires. The performance of the IC was mainly dependent on the transistor population in the past. However, as the complexity of the IC has increased, the interconnect signal delay (RC delay), wire cross-talk and dissipation of energy become major problems for its further improvement.<sup>1</sup> In this context, there has been a growing need for the development of new insulating materials replacing silicon dioxide to overcome these interconnect performance limitations.<sup>2</sup>

Among the low dielectric materials developed for interconnect fabrication, the most notable are silsesquioxane based materials and organic polymers. Polysilsesquioxanes (SSQ) are organosilicates, in which the organic groups provide a low density and low dielectric properties to the silicate. The dielectric property can be further improved by introducing pores into the organosilicate. Porous SSQs have been prepared by using organic polymer templates.<sup>3-9</sup> For example, Yang and coworkers used amphiphilic triblock copolymers, poly(ethylene oxide)-b-poly(propylene oxide)-b-poly(ethylene oxide) (PEO-b-PPO-b-PEO) as a template to generate nanoporous structures.<sup>5</sup> However, the SSOs generally suffer from drawbacks, such as a lack of sufficient toughness and the difficulty of pore structure control. The latter is closely related to reliability issues.

A number of organic polymers have been proposed as future generation dielectric materials.<sup>1,10-13</sup> The most thoroughly evaluated polymer is SiLK (Dow Chemical Co.).1 SiLK is an aromatic thermosetting polymer, having cyclopentadienone and acetylene moieties as reactive groups. SiLK has good dielectric and mechanical properties, but some disadvantages such as its high curing temperature of above 400 °C and synthetic difficulty. Film shrinkage was observed after cross-linking reaction at such a high temperature.<sup>14,15</sup> Poly(binaphthylene ether)s,<sup>10,11</sup> polymers having triptycene units<sup>12</sup> and aromatic polymers having ethynyl units<sup>13</sup> have been also reported as low dielectric polymers.

In the present study, we report novel low dielectric materials based on cyclotriphosphazenes. The cyclotriphosphazenes with skeletal nitrogen and phosphorus atoms exhibit unusual thermal properties such as flame retardancy and self-extinguishibility.<sup>16</sup> Flame retardants are indispensable in the fabrication of electronic devices. Halogen free fire resistant materials for printed circuit boards and IC encapsulators have already become a big issue in the industry.<sup>17,18</sup> Since most organic polymers produce toxic chemicals under fire in a different way from inorganic materials, the flame retardancy of low dielectric constant polymers could be another challenge for their practical application.

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Cyclotriphosphazenes have been incorporated into organic polymers as additives or pendants to improve their thermal properties.<sup>19–22</sup> Thermally curable cyclotriphosphazenes bearing acetylenic,<sup>23</sup> maleimido,<sup>24</sup> and nadic<sup>25</sup> were also reported to produce cross-linked polymer matrices. However, there are few reports concerning dielectric properties of the polymers based on cyclotriphosphazenes. In one early study, a cyclotriphosphazene bearing acryloyloxyethyleneoxy and trifluoroethoxy groups as polymerizable groups and cosubstituents, respectively, was investigated, but the resulting cross-linked polymer showed a very high dielectric constant and poor thermal stability, probably due to its polar and flexible organic groups.<sup>26</sup> Polar polymers have an asymmetric charge distribution, and thus higher dielectric constant and dielectric loss values.

## **Results and discussion**

#### Monomer synthesis

We prepared thermally curable cyclotriphosphazenes containing acetylene and styrene groups according to Scheme 1. 4'-Trimethylsilylethynyl-1,1'-biphenyl-4-ol was synthesized by reaction of 4'-bromo-1,1'-biphenyl-4-ol with (trimethylsilyl)acetylene using a palladium catalyst. Six chloro groups of hexachlorocyclotriphosphazene were replaced by reaction with sodium salts of 4'-trimethylsilylethynyl-1,1'-biphenyl-4-ol. Trimethylsilyl groups were removed under basic conditions to give cyclotriphosphazene 1 containing acetylene groups. Heterosubstituted cyclotriphosphazene 2 was prepared using 4-phenylphenol as a cosubstituent. Substitution mole percentage of the acetylene compound was controlled to be about 40%. In the similar manner, 4-hydroxystyrene was introduced to the cyclotriphosphazene ring to result in compound **3**. All six chloro groups of hexachlorocyclotriphosphazene were substituted by the sodium salt of 4-hydroxystyrene.

#### Thermal polymerization

Thermal polymerization of compounds 1-3 was examined by DSC. Thermograms were obtained by scanning the sample twice from 30 °C to 350 °C with a heating rate of 10 °C min<sup>-1</sup> under nitrogen atmosphere. Homosubstituted cyclotriphosphazene 1 showed strong exotherms for the thermal reaction of acetylene groups above 175 °C, while heterosubstituted cyclotriphosphazene 2 showed a sharp endotherm for melt transition at 200 °C, immediately followed by a strong exotherm. In the second scan, no significant exothermic peaks appeared, indicating that most acetylene groups were thermally reacted in the first scan (Fig. 1a). Highly cross-linked polymers were obtained by thermal polymerization of cyclotriphosphazenes 1 and 2 at 200 °C for 2 h. They showed excellent thermal stability. The 5% weight loss temperatures  $(T_{d5})$  of the cross-linked polymers of compounds 1 and 2, measured by TGA under nitrogen, were 523 and 480 °C, respectively (Fig. 1b). The IR spectra of compounds 1 and 2 showed the peaks for C-H and C-C triple bond stretching modes of the acetylene groups at 3293 and 2107 cm<sup>-1</sup>, respectively. After polymerization, these peaks almost disappeared. The acetylene group has been widely used as a cure site



Scheme 1 Synthesis of thermally curable cyclotriphosphazenes.



Fig. 1 (a) DSC and (b) TGA thermograms of 1 and 2.

because it is thermally curable without the evolution of volatiles. It has been proposed that several reactions are involved in the curing process, including cyclotrimerization to an aromatic ring structure, biradical reaction to form linear or cyclic conjugated linkages, coupling reaction to form diyne structures and Diels–Alder reactions to form condensed polycyclic aromatic structures.<sup>27,28</sup>

Styrene containing cyclotriphosphazene 3 showed a sharp melt transition peak around 100 °C and a broad exothermic peak for the thermal polymerization of styrene groups above 150 °C in the DSC thermogram. No peak appeared in the second scan (Fig. 2a). The spontaneous thermal polymerization of styrene has been well known for many years. Although the mechanism of the polymerization has not been fully understood, it is generally accepted that the dimerization of styrene is involved in the initiation step.29 The dimerization may proceed via a Diels-Alder type [2 + 4] addition or an addition between two vinyl groups. Both reactions produce radicals, which will initiate the polymerization of styrene. Six membered or four membered cyclic adducts can be also formed by the reactions. The polymer obtained by thermal polymerization of cyclotriphosphazene 3 at 150 °C for 2 h also showed good thermal stability with a  $T_{d5}$  of 472 °C (Fig. 2b).

We prepared copolymers of cyclotriphosphazene 3 with styrene. Polystyrene is known as an excellent insulator but

cannot tolerate elevated temperatures. The polymerization was carried out by UV irradiation (a high pressure mercury arc lamp, 3 mW cm<sup>-2</sup>) in the presence of a photoinitiator (2,2-dimethoxy-2phenylacetophenone) at room temperature, resulting in the highly cross-linked, thermally stable cyclotriphosphazene embedded polystyrene. Thermal properties of the copolymers were investigated by DSC and TGA (Fig. 2c and 2d). As the proportion of compound **3** was increased from 5 to 20 wt%, the  $T_g$  of the copolymer was also increased. When the content of compound **3** was above 20 wt%, no discernible glass transition was found. In the TGA thermograms, the copolymers showed good thermal stability nearly comparable to the homopolymer of compound **3** when its composition was higher than 60%.

The IR spectrum of compound **3** showed the C==C stretching vibration peak of the styrene units at 1629 cm<sup>-1</sup>. Based on the peak intensity decrease, the conversions were estimated to be about 70% in the homopolymerization of compound **3** and nearly 100% in the copolymerization of compound **3** and styrene. The high conversion in the copolymerization was attributable to the fact that the reaction of the styrene units of compound **3** with styrene monomers occurred in addition to the inter- and intra-molecular reactions between themselves.

Flame-retardant property. The flame-retardant property of the polymers was evaluated by measuring LOI (limiting oxygen



Fig. 2 (a) DSC and (b) TGA thermograms of 3 and (c) DSC and (d) TGA thermograms of the copolymers of 3 and styrene.

Monomer	Dielectric constant (at 1 GHz)	Dielectric Loss (at 1 GHz)	$T_{\rm g}/^{\circ}{\rm C}$	$T_{\rm d5}/^{\circ}{\rm C}$	LOI (%)	Char yield $(\%)^b$
1	3.12	0.0016	_	523	52	85
2	3.07	0.0020		480	50	74
3	2.40	0.0014		472	49	63
Styrene/3 (10 wt%)	2.55	0.0041	109	310	21	8
Styrene/3 (20 wt%)	2.53	0.0038	139	353	22	16
Styrene/3 (40 wt%)	2.58	0.0019		364	24	31
Styrene/3 (60 wt%)	2.58	0.0015		388	27	42
<sup><i>a</i></sup> DSC and TGA were	carried out at a heating rate of 10 °C	min <sup>-1</sup> . The $T_{d5}$ indicates a 5% wei	ght loss tem	perature. <sup>b</sup> M	leasured at 700	°C under nitrogen.

 Table 1
 The dielectric and thermal properties of the polymers<sup>a</sup>

index) values according to an ASTM D2863 method. The polymers of cyclotriphosphazene **1** containing six acetylene groups and cyclotriphosphazene **2** having mixed substituents of acetylene (40%) and phenylphenoxy (60%) groups showed very high LOI values of 52 and 50, respectively. The polymer of compound **3** with styrene groups also exhibited a high LOI value of 49. The copolymers of compound **3** and styrene showed an improved flame retardancy compared with polystyrene (LOI = 18.8).<sup>30</sup> Their LOI values increased in accordance with the increase of the content of compound **3**. Char yields of the polymers showed a similar trend to the LOI values. The polymer of compound **1** had the highest char yield of 85% at 700 °C under nitrogen, while the polymers of compounds **2** and **3** showed a little lower char yields of 74% and 63%, respectively. Thermal properties of the polymers are summarized in Table 1.

## **Dielectric properties**

Polymer pellets with a thickness of 1–2.5 mm were prepared for dielectric constant and dielectric loss measurements. Compounds 1–3 were placed in a Teflon molder and polymerized thermally or photochemically as described above. Air was removed from the pellet by applying gentle pressure during the polymerization. No macro pores were found in the cross-section, which was examined by SEM (Fig. 3). The pore structure will decrease the dielectric constant but also cause problems such as interconnection and deterioration of the mechanical property.

The dielectric properties of the polymers were measured by a metal-insulator-metal method.<sup>31</sup> The polymer obtained from acetylene containing cyclotriphosphazene **1** and **2** showed



**Fig. 3** SEM image of cross-section of the specimen prepared by polymerization of compound **3**.

dielectric constant of about 3.12 and 3.07, respectively, at 1 GHz. Much improved dielectric properties were obtained from the styrene containing cyclotriphosphazene systems. The polymer of cyclotriphosphazene **3** showed a dielectric constant of 2.40 and a dielectric loss of 0.0014 at 1 GHz. This dielectric constant value is lower than those of SiLK (2.65)<sup>1</sup> and polystyrene (2.6).<sup>32</sup> We presume that the hypercross-linked network structure increased the free volume of the polymer and lowered the dielectric constant.<sup>33</sup> The dielectric properties of the polymers are summarized in Table 1. The polymer of compound **3** showed hardness of 0.31 GPa, which was similar to that of SiLK (0.38 GPa).<sup>1</sup>

Fig. 4 shows dielectric constants and dielectric losses of the homo and copolymers of compound **3** having different compositions, measured according to electric frequency. In proportion to the amount of compound **3** in the copolymers, dielectric constants did not change significantly, but dielectric losses decreased. It showed an especially sharp fall of a dielectric loss when the content of compound **3** was larger than 20 wt% in the copolymer. The dielectric constant and dielectric loss values of the homopolymer and the copolymers of compound **3** were almost constant from 0.1 to 1 GHz.

# Conclusions

We developed curable cyclotriphosphazenes as low dielectric materials. In particular, the polymers of compound **3** bearing styrene groups showed excellent dielectric properties; low dielectric constant and dielectric loss over the range of 0.1 to 1 GHz. The dielectric and physical properties of the polymers could be controlled without sacrificing much thermal stability through the copolymerization with styrene. We expect these cyclotriphosphazenes will be useful as future low dielectric materials.

# Experimental

### Measurements

<sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P nuclear magnetic resonance (NMR) spectra were measured by a Bruker Avance DPX-300 (300 MHz for <sup>1</sup>H NMR) spectrometer and a Bruker Avance DPX-500 (200 MHz for <sup>31</sup>P NMR) spectrometer. All chemical shifts were listed in ppm downfield from tetramethylsilane (<sup>1</sup>H NMR) and phosphoric acid (<sup>31</sup>P NMR). Fourier transform infrared (FT-IR) measurements were recorded on a PERKIN ELMER Spectrum GX I using KBr pellets. Elemental analyses were performed by an EA



Fig. 4 (a) Dielectric constants and (b) dielectric losses of the polymer of compound 3 and the copolymers of compound 3 and styrene.

1110 (CE Instrument) and a Flash 1112 (Thermo Electron corporation). Dielectric constant and dielectric loss were measured by a metal-insulator-metal method using an E4991A RF impedance/material analyzer (Agilent Technology). The frequency ranged from 1 MHz to 1 GHz. Thermogravimetric analysis (TGA) was performed on a TA modulated TGA2050 with a heating rate of 10 °C min<sup>-1</sup> under nitrogen. Differential scanning calorimetry (DSC) measurement was performed by a TA modulated DSC Q10 with a scanning rate of 10 °C min<sup>-1</sup> under nitrogen. SEM images were obtained by using a JEOL JSM-6330F microscope. Hardness was determined with a nanoindenter (AIS2100, Frontics. Inc.) according to the reported procedure.34 LOI (limiting oxygen index) values were measured by a Fire Testing Technology instrument at a flow rate of 10.6 L min<sup>-1</sup> with test specimen bars of 80 mm in length, 10 mm in width and about 4.0 mm in thickness. The testing was performed according to American Society for Testing and Materials (ASTM) test D2863.

#### Synthesis and characterization

4'-Trimethylsilylethynyl-1,1'-biphenyl-4-ol. 4'-Bromo-1,1'biphenyl-4-ol (10.0 g, 40.5 mmol) was dissolved in TEA (200 ml). To the solution dichlorobis(triphenylphosphine)palladium (1.13 g, 1.62 mmol) and copper iodide (0.153 g, 0.81 mmol) were added. After stirring for 1 h at room temperature, (trimethylsilyl)acetylene (4.70 g, 0.48 mmol) was added and the resulting solution was stirred for 20 h at 40 °C. After filtration and evaporation, the product was isolated by column chromatography on silica gel (9% ethyl acetate in hexane) (8.90 g, 84%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.38–7.54 (m, 6H, Ar), 6.89 (d, 2H, Ar), 0.24 (s, 9H, -Si(CH<sub>3</sub>)<sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 156.0, 140.9, 132.5, 128.5, 126.5, 121.6, 115.9, 105.3, 94.8. IR (KBr): 3400, 2160, 1610, 1495, 1250. Anal. calcd for C<sub>17</sub>H<sub>18</sub>OSi: C, 76.64; H, 6.81. Found: C, 76.78; H, 6.53%.

N<sub>3</sub>P<sub>3</sub>(OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>C ≡ CSiMe<sub>3</sub>)<sub>6</sub>. Sodium hydride (0.50 g, 21.0 mmol) was added to a solution of 4'-trimethylsilylethynyl-1,1'biphenyl-4-ol (5.50 g, 21.0 mmol) in tetrahydrofuran (100 ml). After stirring for 1 h at room temperature, a solution of hexachlorocyclotriphsphazene (1.00 g, 2.88 mmol) in tetrahydrofuran (50 ml) was added dropwise and refluxed for 48 h. The solvent was removed by evaporation and the product was isolated by column chromatography on silica gel (50% tetrahydrofuran in hexane) (4.25 g, 85%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.46–7.49 (d, 12H, Ar), 7.25–7.32 (m, 24H, Ar), 6.94–7.05 (d, 12H, Ar), 0.24 (s, 54H, -Si(CH<sub>3</sub>) <sub>3</sub>). <sup>13</sup>C NMR (CDCl<sub>3</sub>): δ 150.4, 140.2, 137.1, 132.9, 128.1, 126.7, 121.7, 115.9, 105.3, 94.8. <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  9.79. Anal. calcd for C<sub>102</sub>H<sub>102</sub>N<sub>3</sub>O<sub>6</sub>P<sub>3</sub>Si<sub>6</sub>: C, 70.92; H, 5.95; N, 2.43. Found C, 71.01; H, 5.53; N, 2.47%.

 $N_3P_3(OC_6H_4C_6H_4C \equiv CH)_6$  (1). To a solution of hexakis(4'trimethylsilylethynyl-1,1'-biphenyl-4-oxy)cyclotriphosphazene (4.25 g, 2.40 mmol) in tetrahydrofuran (100 ml) and methanol (30 ml), potassium hydroxide (1.30 g, 22.0 mmol) was added. After stirring for 3 h at room temperature, the solvents were removed by evaporation. The resulting residue was dissolved in ethyl acetate (50 ml). The solution was washed with water (50 ml) and dried over anhydrous magnesium sulfate. After filtration and evaporation, the product was isolated by column chromatography on silica gel (50% tetrahydrofuran in hexane) (3.0 g, 97%). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.46–7.49 (d, 12H, Ar), 7.25– 7.32 (m, 24H, Ar), 6.94-7.05 (d, 12H, Ar), 3.15 (s, 3H,  $-C \equiv CH$ ). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  150.4, 140.2, 137.1, 132.9, 128.1, 126.7, 121.7, 115.9, 83.5, 78.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 9.79. Anal. calcd for C<sub>84</sub>H<sub>54</sub>N<sub>3</sub>O<sub>6</sub>P<sub>3</sub>: C, 77.95; H, 4.21; N, 3.25. Found C, 77.68; H, 4.20; N, 2.99%.

 $N_3P_3(OC_6H_4C_6H_4C \equiv CSiMe_3)_{2,4}(OC_6H_4C_6H_5)_{3,6}$ Sodium hydride (0.41 g, 17.40 mmol) was added to a solution of 4-phenylphenol (3.00 g, 17.40 mmol) in 1,4-dioxane (50 ml). After stirring for 1 h at room temperature, a solution of hexachlorocyclotriphosphazene (2.00 g, 5.75 mmol) in 1,4-dioxane (50 ml) was added dropwise. After refluxing for 24 h, a solution of sodium 4'-trimethylsilylethynyl-1,1'-biphenyl-4oxide, prepared from 4'-trimethylsilylethynyl-1,1'-biphenyl-4-ol (5.60 g, 20.1 mmol) and sodium hydride (0.50 g, 20.1 mmol) in 1,4-dioxane (50 ml), was added to the solution and refluxed for 48 h. After filtration and evaporation, the product was isolated by column chromatography on silica gel (15% ethyl acetate in hexane) (5.29 g, 64%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.44–7.47 (overlap, 7H, Ar), 7.26-7.36 (overlap, 43H, Ar), 6.99-7.03 (m, 15H, Ar), 0.24 (s, 27H,  $-Si(CH_3)$  3). <sup>13</sup>C NMR (CDCl<sub>3</sub>):  $\delta$  150.2, 141.5, 132.8, 128.3, 127.6, 127.0, 126.8, 121.6, 83.6, 78.3. <sup>31</sup>P NMR (CDCl<sub>3</sub>): δ 9.82.

N<sub>3</sub>P<sub>3</sub>(OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>4</sub>C≡CH)<sub>2.4</sub>(OC<sub>6</sub>H<sub>4</sub>C<sub>6</sub>H<sub>5</sub>)<sub>3.6</sub> (2). This compound was prepared by following the procedure for the preparation of compound 1. The product was isolated by column chromatography on silica gel (15% ethyl acetate in hexane) (3.82 g, 92%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.44–7.47 (overlap, 7H, Ar), 7.26–7.36 (overlap, 43H, Ar), 6.99–7.03 (m, 15H, Ar), 3.15 (s, 3H, -C≡CH). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  9.82.

**1,1,3,3,5,5-Hexakisstyreneoxycyclotriphosphazene (3).** 4-Hydroxystyrene was prepared according to the literature procedure.<sup>35</sup> To a solution of 4-hydroxystyrene (8.16 g, 68.0 mmol) in tetrahydrofuran (100 ml), sodiumhydride (1.63 g, 68.0 mmol) was added. After stirring 1 h at room temperature, a solution of hexachlorocyclotriphsphazene (2.60 g, 7.47 mmol) in tetrahydrofuran (50 ml) was added dropwise and stirred for 48 h at 50 °C. After evaporation, the product was purified by recrystallization from methanol (4.72 g, 73%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.16 (d, 2H), 6.83 (d, 2H), 6.60–6.66 (q, 1H), 5.66 (d, 1H), 5.23 (d, 1H). <sup>31</sup>P NMR (CDCl<sub>3</sub>):  $\delta$  9.40. IR (KBr): 3080, 1600, 1503. Anal. calcd for C<sub>48</sub>H<sub>42</sub>N<sub>3</sub>O<sub>6</sub>P<sub>3</sub>: C, 67.84; H, 4.98; N, 4.94. Found C, 67.80; H, 4.97; N, 4.94%.

**Polymerization.** Cyclotriphosphazene compounds were placed in a Teflon mold and heated at 200 °C (for 1 and 2) or at 150 °C (for 3) for 2 h under gentle pressure. The typical procedure of the copolymerization of compound 3 with styrene is as follows: compound 3 (0.056 g,  $6.60 \times 10^{-2}$  mmol) was dissolved in styrene (1.0 g, 8.3 mmol). After addition of 2,2-dimethoxy-2-phenylacetophenone (1.70 mg,  $6.64 \times 10^{-2}$  mmol), the resulting solution was irradiated by a UV lamp (a high pressure mercury arc lamp, 3 mW cm<sup>-2</sup>) for 2 h at room temperature.

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