# Phosphazene Monomers from the Regiospecific Reaction of *tert*-Butylhydroquinone with Hexachlorocyclotriphosphazene: A New Composite Material Precursor

#### FREDERICK F. STEWART, MASON K. HARRUP

Idaho National Engineering and Environmental Laboratory, Lockheed Martin Idaho Technologies Company, P.O. Box 1625, Idaho Falls, Idaho 83415-2208

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**ABSTRACT:** A new synthesis of a phosphazene-based polymer precursor is described. *tert*-Butylhydroquinone was found to react with hexachlorocyclotriphosphazene in the presence of a base, 4-picoline, in cyclohexane to yield a regiospecifically substituted hexa-*tert*-butylcyclotriphosphazene. This reaction proceeds more rapidly to completion and in a higher yield than data previously reported for analogous cyclotriphosphazenes. Nuclear magnetic resonance spectroscopy and thermal methods (differential scanning calorimetry and thermogravimetric analysis) were employed to characterize this material, and it is observed that the bifunctional *tert*-butylhydroquinone substitutes only at the least hindered phenolic hydroxyl under the reported reaction conditions. This conclusion clarifies published data that suggests that without the *tert*-butyl substituent on the hydroquinone ring, crosslinking between phosphazene rings occurs to some extent. © 1999 John Wiley & Sons, Inc. J Appl Polym Sci 72: 1085–1090, 1999

Key words: composites; polymers; phosphazenes; synthesis; cyclomatrix

# **INTRODUCTION**

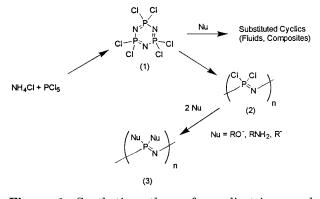
Research into new materials for use in ever expanding technological applications must be tempered by the need for conservation of environmental and natural resources. Likewise, benign alternatives to current processes have become highly desirable. In this article, a new phosphazenebased composite monomer synthesis will be discussed that was designed to be significantly less hazardous than an existing process.

Polyphosphazenes are a class of inorganic polymers that have alternating phosphorus and nitrogen atoms in the backbone. Backbones are also characterized by alternating double and single bonds. It should be noted that the  $\pi$  electrons of the double bonds are not completely delocalized; there is a node at phosphorus that prevents total electron delocalization along the polymer backbone. Thus, this class of polymer is not electronically conducting and is considered to be a good candidate for composite materials. Additionally, polyphosphazenes, because of the inorganic backbone, exhibit a high level of chemical and thermal stability. For example, poly(bisphenoxy)phosphazene has been reported to be stable in excess of 300°C.<sup>1</sup> Glass transition temperatures for polyphosphazenes vary widely, from approximately -84 to  $100^{\circ}C^2$  primarily due to the pendant groups attached to each phosphorus. Phosphorus atoms in the backbone are pentavalent

Correspondence to: F. F. Stewart.

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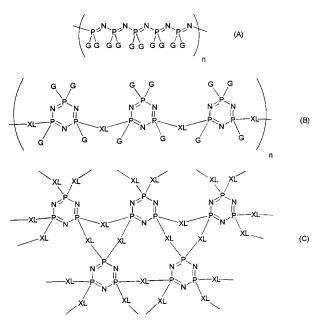


**Figure 1** Synthetic pathway for cyclic trimer and linear phosphazene materials.

allowing for the attachment of two substituent pendant groups. Phosphazenes are generally synthesized<sup>3</sup> from ammonium chloride and phosphorus pentachloride (see Fig. 1). The result of this chemistry is not a polymeric species but a sixmembered phosphorus and nitrogen ring with characteristic phosphazene bonding and two chlorines per phosphorus, hexachlorocyclotriphosphazene, 1. Hexachlorocyclotriphosphazene, 1, a commercially available material, is hydrolytically unstable; however, it readily reacts along two possible pathways. The first pathway is ringopening polymerization<sup>4</sup> to form linear poly(dichloro)phosphazene, 2, with measured molecular weights as high as 2,000,000 (measurement of molecular weight was performed on hydrolytically stabilized fully substituted linear polymers).<sup>5</sup> Poly(dichloro)phosphazene, **2**, is also hydrolytically unstable; however, the polymer backbone may be stabilized by reaction with organic nucleophiles forming polyorganophosphazenes, 3. Reported nucleophiles for the formation of pendant groups are diverse; phenols, alcohols, amines, and organometallic species are among the more commonly examined groups.<sup>6</sup> Uses for polyorganophosphazenes, 3, include membranes for the selective removal of volatile organic chemicals (VOCs) from water,7 VOCs from other organic matrices,<sup>8</sup> and for mixed gas separations.<sup>9,10</sup> In addition, these materials have the potential to be used as flame retardants,  $^{11,12}$  med-ical devices,  $^{13}$  and ionic conductors.  $^{14,15}$  The utility of these materials is dictated by the choice of pendant group.

The second reaction pathway for hexachlorocyclotriphosphazene, 1, concerns direct nucleophilic substitution forming organocyclotriphosphazenes. Substitution versatility witnessed in the linear polymer described above is mirrored in this chemistry. A wide variety of cyclics have been reported.<sup>16</sup> Diverse physical characteristics observed for these materials include crystalline solids<sup>16</sup> as well as low-viscosity fluids.<sup>17</sup> Additionally, organocyclotriphosphazenes may be crosslinked to form two differing polymer backbone configurations, cyclomatrix<sup>18</sup> and cyclolinear.<sup>19</sup> It should be emphasized that the six-membered ring structure of the phosphazene remains intact during crosslinking polymerizations of this nature. Differences in how these rings are joined constitute the cyclomatrix and cyclolinear arrangements (see Fig. 2).

Structural composites have been reported<sup>20</sup> using organocyclotriphosphazenes in a cyclomatrix orientation. An report<sup>21</sup> detailed the synthesis of hexahydroquinonecyclotriphosphazene prepolymer materials based upon an earlier patent.<sup>22</sup> The term prepolymer was employed because hydroquinone, a bifunctional organic nucleophile, has the capability of crosslinking phosphazene rings, and it was not clear to the authors the extent to which this occurs during the synthetic process. Thus, the terms cyclotriphosphazene and cyclic trimer were avoided because these imply



**Figure 2** Polyphosphazene backbone configuration: (A) linear chain; (B) cyclolinear configuration; (C) cyclomatrix configuration. XL = a bifunctional crosslinking group; G = a nucleophilic substituent.

that the product was a discrete molecule. In our laboratory, the issue of the structure of these composite precursors required clarification.

# **EXPERIMENTAL**

#### General

Thermal analyses were performed using a TA Instruments Model 2910 differential scanning calorimeter (DSC) and a TA Instruments Model 2980 thermogravimetric analyzer (TGA). Nuclear magnetic resonance (NMR) analyses were performed on a Bruker AC-300P spectrometer operating at a magnetic field strength of 7.04T (300 MHz, hydrogen). Proton spectra referencing was provided by the residual protons in deuterated acetone solvent (Cambridge Isotopes). <sup>31</sup>P spectra (121 MHz) were referenced to  $85\%~H_3PO_4$  (internal, coaxial), with positive shifts recorded downfield of the reference. <sup>13</sup>C-NMR spectra were acquired at 75.4 MHz and referenced to the  $d_6$ acetone carbonyl carbon (206.0 ppm). Hexachlorocyclotriphosphazene was purchased from Strem Chemicals, Inc. and was purified by sublimation prior to use. Tert-butylhydroquinone and 4-picoline were purchased from Aldrich Chemical Co. and were used as received. Cyclohexane was acquired from Aldrich and freshly distilled from anhydrous calcium carbonate before use.

## Synthesis of Hexa-*tert*butylhydroquinonecyclotriphosphazene (4)

A 2-L, three-neck, round-bottom flask was charged with 102 g (0.61 mol) of *tert*-butylhydroquinone, 21.4 g (61 mmol) of hexachlorocyclotriphosphazene, and 800 mL of cyclohexane. The flask was then fitted with a reflux condenser and a 100 mL pressure equalizing addition funnel and a mechanical stirrer. All remaining openings were sealed with rubber septum stoppers. The experimental apparatus was purged with dry nitrogen for 30 min. 60 mL (0.61 mol) of 4-picoline was added to the addition funnel by syringe, and the 10-fold excess allows for neutralization of HCl generated during synthesis. The 4-picoline was added dropwise to the reaction mixture over approximately 5 min. The resulting mixture was heated at reflux for 4 h with stirring, upon which two phases were observed. The upper phase was clear, and the lower phase was orange colored and

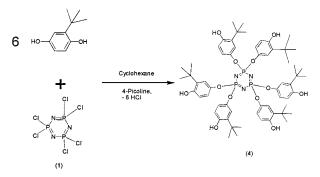
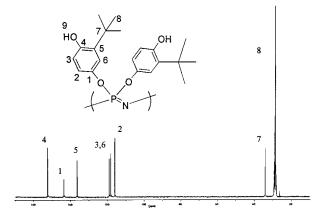


Figure 3 Synthesis of hexa-*tert*-butylhydroquinone-cyclotriphosphazene.

viscous. The reaction was cooled overnight under nitrogen. At this time, the lower phase solidified, allowing the upper phase to be decanted. The lower phase was treated with 80% aqueous acetic acid and stirred with mild heating until the entire residue was dissolved. The acidic solution was poured into 3 L of room-temperature, deionized water to give an off-white solid that was collected by suction filtration. The residue was transferred to a cellulose Soxhlet thimble and extracted with water for 2 days. Upon drying under vacuum, 69.2 g of hexa-*tert*-butylhydroquinonecyclotriphosphazene was obtained in an 81% yield.

## DISCUSSION

Characterization of the solid product formed from the reaction of tert-butylhydroquinone with hexachlorocyclotriphosphazene (Fig. 3) was performed using NMR, DSC, and TGA. A <sup>13</sup>C-NMR spectrum (Fig. 4) was collected at room temperature from dilute deuterated acetone solutions, and eight unique resonances could be assigned to the product, as shown in Table I. In the aromatic region of the spectrum, three methine carbons are observed corresponding to the three on the tertbutylhydroquinone ring. Additionally, three nonprotonated resonances are observed. The farthest downfield peak at 152.4 ppm has been assigned to the free phenolic carbon, and this agrees well with the data reported for the simple hydroquinone cyclic trimer (155 ppm). Likewise, the peak at 143.5 ppm is assigned to the phosphorus-bound phenol carbon corresponding well with published data (144 ppm). The remaining resonance at 136.4 ppm is assigned to the *tert*-butyl bearing carbon. <sup>31</sup>P-NMR data for this new trimer is far



**Figure 4** <sup>13</sup>C-NMR spectrum of hexa-*tert*-butylhyd-roquinonecyclotriphosphazene.

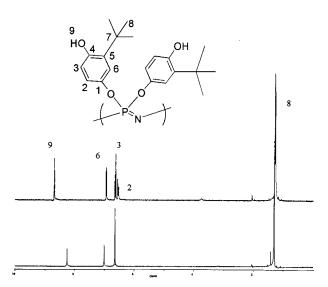
simpler with one singlet observed at 10.3 ppm, again in good agreement with published data (11.7 ppm).

Proton NMR spectra collected at room temperature gave ambiguous data (see Fig. 5). In the aromatic region, three singlets were observed that integrated to four protons; no coupling information was observed (see Fig. 3). Data acquired at 240K revealed the coupling information between the aromatic protons, two doublets, and a double of doublets. The doublet of doublets at 6.54 ppm is assigned to the proton *ortho* to the phosphorus bearing phenolic site, proton 2, with the larger coupling due to the  $\alpha$ -proton, 6.64 ppm (proton 3), and the smaller coupling due to other ortho proton, 6.94 ppm (proton 6). These assignments leave the tert-butyl group meta to the phosphorus-bearing phenolic site (carbon 4). To give further support to these assignments, different nuclear Overhauser effect (NOE) experiments

 Table I
 Proton and Carbon NMR Data for

 Hexa-tert-butylhydroquinonecyclotriphosphazene

	<sup>1</sup> H-NMR (ppm)	<sup>13</sup> C-NMR (ppm)
1	_	143.5
<b>2</b>	6.54 (dd 8.72, 2.57 Hz)	116.0
3	6.64 (d 8.72 Hz)	118.1
4	_	152.4
5	_	136.4
6	6.94 (d 2.57 Hz)	119.0
7	_	34.1
8	1.30 (s)	28.7
9	8.68 (s)	—



**Figure 5** Proton NMR data of hexa-*tert*-butylhydroquinonecyclotriphosphazene. A lower spectrum was obtained at room temperature. An upper spectrum was acquired at 240 K.

were performed. A clear NOE enhancement of 2.4% was measured between the free phenolic hydroxyl proton, 8.68 ppm (proton 9), and proton 3, 6.64 ppm. A weaker enhancement of 0.4% was measured between the free phenolic proton 9 and the *tert*-butyl protons, suggesting that the *tert*butyl group has a large steric influence over the conformation of the hydroxyl group, forcing it away from the *tert*-butyl group toward proton 3. An additional enhancement was measured at 5.2% between the *tert*-butyl protons and proton 6, indicating their close proximity. Further support for the assignments of both carbon and protons was provided through the use of standard twodimensional correlation spectroscopy techniques (COSY and HETCORR). These data firmly establish the stereospecific regiochemistry of hydroquinone attachment to the phosphazene ring, as drawn in Figure 5.

DSC analysis of the material performed from -150 to  $400^{\circ}$ C revealed three key features. The first was an endotherm between 49 and  $67^{\circ}$ C, corresponding to annealing. Secondly, a sharp endotherm at  $188^{\circ}$ C was indicative of melting. Finally, thermal decomposition was observed to commence at  $230^{\circ}$ C with an initial exotherm that turns strongly endothermic as the decomposition proceeds. Residues after the experiment was completed were visually inspected, and the trimer

was found to be decomposed into a black powder. A TGA experiment revealed four major features. Steady but minor weight loss was observed with a total of 8% by 200°C, which can be interpreted as loss of volatile components occluded in the bulk sample. A sharper weight loss at approximately 180°C corresponds well with the melt transition observed by DSC, which suggests an accelerated loss of volatile components during this transition. Between 260 and 320°C, 8% more of the sample is lost due to thermal decomposition. The apparent rate of weight loss increases above 320°C until approximately 425°C, with a weight loss of an additional 30%, representing the bulk of the decomposition process. These data correspond well with data reported for the hydroquinone analogue, although the temperature at which the decomposition occurs is somewhat lower for this new trimer. Possible explanations include the definite discrete nature of the new material and the higher organic content of the tert-butylhydroquinone system due to the tert-butyl groups, which would be expected to decompose at lower temperatures.

### CONCLUSION

The nature of the synthesis of hexa-tert-butylhydroquinonecyclotriphosphazene was investigated. In contrast to previously published reports, tertbutylhydroquinone appears to substitute stoichiometrically with hexachlorocyclotriphosphazene. As shown by NMR spectroscopy, the substitution process occurs regiospecifically with the *tert*-butyl-groups oriented away from the phosphorusnitrogen ring in the product. In addition, no NMR resonances are observed for any other orientation; thus, the structure of this molecule is discretely trimeric, with no observed crosslinking due to reaction of both phenolic sites. Steric hindrance of the hydroxyl group ortho to the tertbutyl group appears to effectively block the site to attachment on the ring, and this preference is reasonable due to the use of a 10-fold excess of *tert*-butylhydroquinone during the synthesis process.

Preliminary investigations are underway that suggest that composites can be effectively formed using this new trimeric phosphazene, and our findings will be reported shortly. These results are encouraging as hydroquinone is listed as a suspected carcinogen while the *tert*butyl derivative is only an irritant; thus, an added measure of safety is incorporated into both the synthesis and the use of this composite material. A further comparison of this process with the hydroquinone system also shows that the observed reaction rates, and yields were observed to be higher with the *tert*-butyl-group substitution on to the hydroguinone ring. Reflected in this result is the higher nucleophilicity of the tert-butylhydroquinone due to increased electron donation into the aromatic ring from the tert-butyl group. Finally, this work clarifies the chemistry of cyclic trimer substitution and suggests that other substituents may be attached similarly to further diversify this polymer precursors obtainable using this improved methodology.

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