Reactions and Polymerization of Hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene: A New Method for the Preparation of Soluble Cyclomatrix Phosphazene Polymers

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ABSTRACT: Novel cyclomatrix phosphazene-containing polyester polymers were synthesized through the reaction of a polyhydroxylated cyclotriphosphazene and a bifunctional acid chloride. To demonstrate the chemistry of the free hydroxyl of hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene, nucleophilic displacement reactions were performed with both acetic anhydride and alkyl chlorides. This work compares favorably to literature data for the chemistry of hexa-[4-hydroxyphenoxy]cyclotriphosphazene, whose hydroxyl is not hindered by an adjacent substituent. The hindered site of hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene was found to react with bidentate acid chlorides to yield new high polymers. The phosphazene-containing polyesters were observed to have good solubility in polar organic solvents. Characterization of these new materials was performed using dilute solution laser light scattering techniques, thermal analysis, and NMR spectroscopy. © 2001 John Wiley & Sons, Inc. J Appl Polym Sci 80: 242–251, 2001

Key words: phosphazenes; cyclomatrix; polyester; cyclotriphosphazenes; hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene

INTRODUCTION

Polyphosphazene polymers are a versatile class of hybrid organic–inorganic materials that have many remarkable properties. The backbone of this polymer consists of alternating phosphorus and nitrogen atoms with alternating double and single bonds. Phosphorus, in this configuration is pentavalent with two substituents on phosphorus. Initially, phosphazene linkages are formed from the condensation of phosphorus pentachloride and ammonium chloride,[1] which yields a colorless crystalline solid that is easily sublimed. Heating of this material yields an elastomer with an empirical formula of $PNCl_2$ that was originally termed "inorganic rubber."[2] This rubber was found to be hydrolytically unstable and evolved hydrochloric acid upon exposure to water. Later, it was recognized that this polymer could be deliberately modified with organic nucleophiles via the labile chlorines. This strategy yields a variety of robust polymers[3] and is still in widespread use.

Soluble and hydrolytically stable phosphazene polymers have a variety of uses including membranes for the removal of water from aqueous solutions,[4] organic separations,[5] and solid polymer electrolytes.[6,7] Additionally, they may be formed as water-soluble high polymers,[6,7] or as

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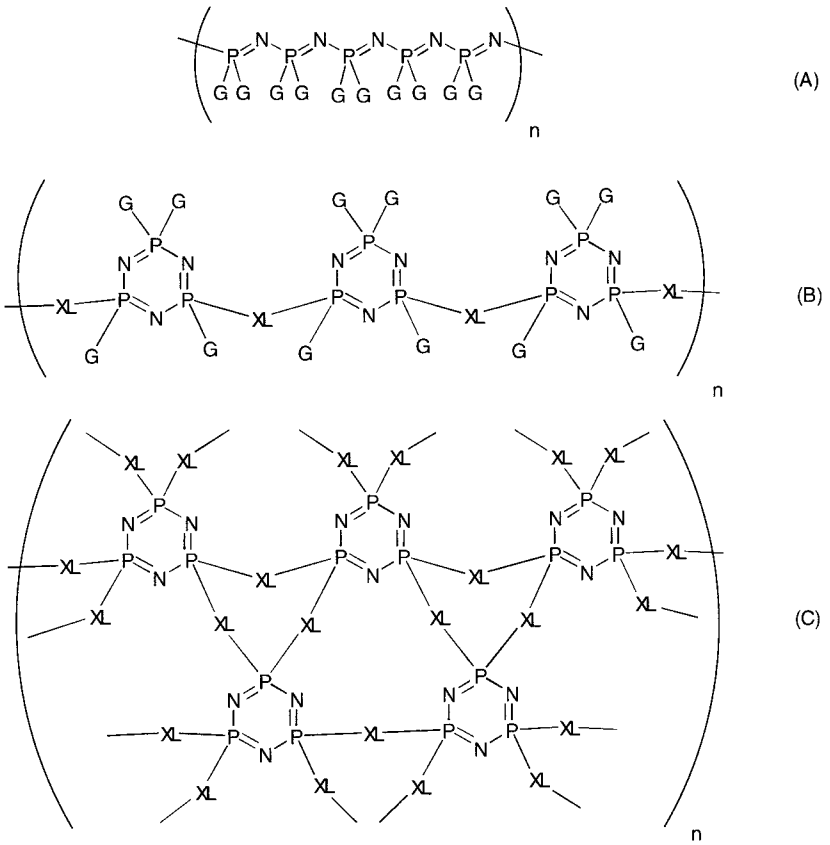


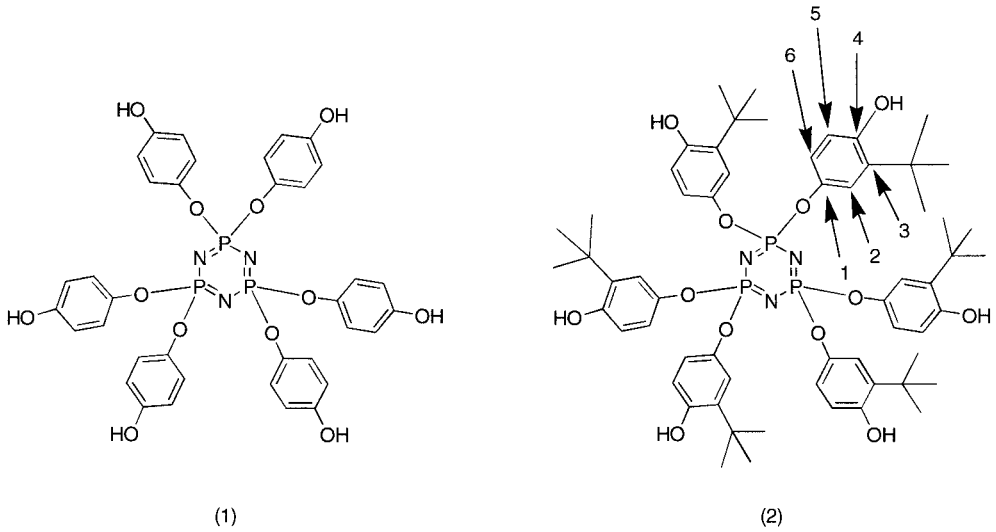
Figure 1 Polyphosphazene backbone configurations. (A) Linear chain. (B) Cyclolinear configuration. (C) Cyclomatrix configuration. XL = A bifunctional crosslinking group. G = nucleophilic substituent.

nonflammable fluids.[8] The key to these polymers is solubility in certain solvents that allows for facile formation of utile materials such as thin dense films. The variety of applications that have been proposed for phosphazene polymers is a clear reflection of diversity of the chemistry that they possess.

Polymerization of phosphazene material potentially can be performed to yield three distinct backbone structures: linear, cyclolinear, and cyclomatrix (see Fig. 1). Of these structures, the linear configuration has been the most extensively studied.[9] Cyclolinear structures have been the least studied due to the complexity of synthesis. Cyclomatrix polyphosphazenes are more common than the cyclolinear structures as there are several synthetically accessible routes and are potentially more useful materials than cyclolinear materials.[10] For example, crosslinked hexa-[4-hydroxyphenoxy]cyclotriphosphazene (**1**) was found to react readily with hexamethylenetetraamine at 200°C to yield a durable but intractable solid structural material.[11] An alternate synthesis[12,13] was reported that employed electrochemical techniques to form films for a variety of purposes.

Uncrosslinked hexa-[4-hydroxyphenoxy]cyclotriphosphazene has been synthesized through a two-step protection–deprotection methodology.[14] This method entailed the synthesis of hexa-[4-methoxyphenoxy]cyclotriphosphazene and hexa-[4-phenoxyphenoxy]cyclotriphosphazene from hexachlorocyclotriphosphazene and the corresponding substituted phenol. Unmasking of the hydroxyl functionality was performed by hydrolysis of the corresponding alkyl or aromatic ether to yield uncrosslinked **1**. ^{31}P NMR characterization of **1** revealed a singlet suggesting a neat uncrosslinked cyclic trimer.

An alternate one-step synthesis of **1** was reported[15,16] as the reaction of hexachlorocyclotriphosphazene with hydroquinone in the presence of pyridine. As the reaction proceeds, the pyridine acts as a base for proton abstraction from the



(1) (2)

Figure 2 Structures of hexa-[4-hydroxyphenoxy]cyclotriphosphazene (**1**) and hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene (**2**).

hydroquinone to produce the active nucleophile that displaces the labile chlorine on the phosphazene ring to yield **1** (see Fig. 2). Characterization of this reaction was performed with ^{31}P NMR spectroscopy where several peaks were observed, suggesting inhomogeneous phosphorus speciation. This result is attributed to reaction of both hydroxyl sites on the hydroquinone resulting in a partially crosslinked structure. Prevention of crosslinking by using an excess of hydroquinone was unsuccessful.

Further work[17] using the one-step method of Femec[16] examined the reaction of *tert*-butylhydroquinone with hexachlorocyclotriphosphazene where a discrete monomeric product was observed, hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene (**2**; see Fig. 2). The ^{31}P NMR spectrum of this molecule showed only one resonance, in contrast to the hydroquinone analogue. It was proposed that using an excess of the *tert*-butylhydroquinone during synthesis, crosslinking of cyclotriphosphazene rings was prevented through the steric hindrance provided by the *tert*-butyl group. Further evidence was collected to support this conclusion via ^{13}C NMR spectroscopy. Attachment of the *tert*-butylhydroquinone to the cyclotriphosphazene ring was shown to occur in a regiospecific manner where the *tert*-butyl group was located exclusively in position 3.

Exploration of the chemistry of the aromatic hydroxyl moiety has been reported by several groups. Inorganic species such as phosphates[18] and silica matrices[19] have been readily attached. Additionally, photoreactive[20] organics and carboxylic acid derivatives[21] have been attached yielding materials with new and interesting properties. In this paper, the chemistry of the hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene was explored with the goal of probing the reactivity of the hindered free hydroxyl group in light of existing literature data and establishing new pathways for the synthesis of soluble cyclomatrix polymers with the potential to be used as thin dense films.

EXPERIMENTAL

General

All NMR spectra were acquired using a either a Bruker AC-300P or a Bruker DMX-300WB spectrometer operating at 300.1 MHz (^{1}H), 75.5 MHz (^{13}C), and 121.5 MHz (^{31}P). All spectra were collected in either acetone-d_6 or toluene-d_8 (Cambridge Isotopes). All ^{13}C and proton NMR spectra were referenced externally to tetramethylsilane. All ^{31}P spectra were referenced to an external H_3PO_4. Glass transition temperatures were determined using a TA Instruments model 2910 differential scanning calorimeter and thermogravimetric analyses (TGAs) were performed using a TA Instruments Model 2950 Thermogravimetric Analyzer. Elemental analysis was performed on Carlo Erba model EA1108 elemental analyzer.

Molecular Weight Characterization

Dilute solution techniques were used to characterize the macromolecular structures of the polymers made in this study. Tetrahydrofuran (THF), filtered through a 0.02 μm filter, was used as solvent, and all experiments were performed at 22°C. Solution refractive index increment (*dn/dc*) values were obtained using a Rainin Dynamax RI-1 differential refractive index detector. The instrument constant was determined via calibration using known concentrations of polystyrene standards whose *dn/dc* values are well known. Laser light scattering (LLS) measurements were made using a Wyatt Technologies Dawn-DSP laser photometer, using polarized light (633 nm) to measure scattered light intensities at 18 angles ranging from 22.5° to 147°. The instrument was calibrated with toluene (Aldrich), which also was filtered through a 0.02 μm filter. Dilute solutions in the 10^{-4} to 10^{-5} g/mL range were prepared for scanning on the LLS instrument. Debye plots were prepared to obtain weight-average molecular weights, *z*-average square radii (mean square radii), and second-virial coefficients. High performance size exclusion chromatography and detection (HPSEC) was performed using a Waters Model 2690 solvent/sample delivery system with a column bank of two Styragel HR 5E (4.6 mm i.d. $\times$ 300 mm) solvent-efficient columns. The columns were kept isothermal at 22°C and operated with a solvent flow rate of 0.3 mL/min. The polymer solutions were filtered through a 0.45 μm filter prior to injection onto the columns. The polymers were detected using the Wyatt Technologies Dawn-DSP laser light scattering detector with the F2 flow cell, which measures scattered light intensities at 16 angles ranging from 12.3° to 165.1°. The refractive index detector described above was placed in series with the light scattering detector as a concentration detector.

Synthesis of Hexa-[4-hydroxyphenoxy]cyclotriphosphazene (1)

This phosphazene was synthesized as described in a previous report.[16] ^{31}P NMR (acetone-d_6) δ 11.4, 11.3, 11.2 ppm. ^{13}C NMR (acetone-d_6) δ 154.6, 143.6, 121.9, 115.9 ppm.

Synthesis of Hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene (2)

This phosphazene was synthesized as described in a previous report.[17]

Reaction of 1 and 2 with Acetic Anhydride to Yield 3 and 4

Compounds **3** and **4** were synthesized using a similar method[14]; the synthesis of **3** is shown here. A 50 mL flask was charged with 2.0 g (2.5 mmol) of **1**, 30 mL of dry 1,4-dioxane, 1.6 mL (16 mmol) of 4-picoline, and a magnetic stirrer. To the reaction mixture was added 1.6 mL (17 mmol) of acetic anhydride and the reaction was stirred under ambient conditions for 2 h under nitrogen atmosphere. The reaction was then heated to reflux for 2.5 h and allowed to cool to room temperature. Isolation of compound **3** was accomplished by quenching the excess anhydride with water followed by extraction of the product into CH_2Cl_2. The product was washed sequentially with three portions of dilute HCl and three portions of dilute aqueous $NaHCO_3$ to yield 0.9 g of a pale yellow solid (34% yield). Hexa-[4-acetyloxyphenoxy]cyclotriphosphazene, **3**: ^{31}P NMR (acetone-d_6) δ 10.6. ^{13}C NMR (acetone-d_6) δ 169.4, 148.7, 148.2, 123.6, 122.2, 20.7. Differential scanning calorimetry (DSC) T_g 69°C. TGA T_d 250°C. Hexa-[4-acetyloxy-3-*tert*-butylphenoxy]cyclotriphosphazene (**4**): ^{31}P NMR (acetone-d_6) δ 9.90 ppm. ^{13}C NMR (acetone-d_6) δ 169.4, 148.4, 147.0, 143.3, 126.1, 119.3, 117.2, 35.0, 30.0, 21.4. ^{1}H NMR (acetone-d_6) δ 7.27, 7.03, 6.84, 2.38, 1.34. DSC T_g 65°C, TGA T_d 370°C. 74% yield.

Reaction of 2 with Alkyl Halides to Yield Compounds 5 and 6

A 500 mL three-neck flask equipped with a water condenser and a magnetic stir bar was charged with **2** (8.1 g, 7.2 mmol) and 1-bromohexane (61 mL, 430 mmol), and dissolved in acetone (200 mL). To the stirring solution, K_2CO_3 (20 g) and KI (0.3 g) were added, and the mixture was heated to reflux under a flow of nitrogen for approximately 5 days. During this time, the reaction was monitored by ^{31}P NMR spectroscopy. When the reaction was complete, the solids were removed by filtration. Acetone in the filtrate was removed using a rotary evaporator followed by vacuum distillation to remove the unreacted 1-bromohexane. The residual oil was chromatographed on a silica gel column using *n*-hexanes:ethyl acetate as the eluent (6:1 by volume). After rotary evaporation of the eluent, a highly viscous honey colored oil was obtained (23% yield). Hexa-[3-*tert*-butyl-4-*n*-hexanoxyphenoxy]cyclotriphosphazene (**5**): ^{31}P NMR (acetone-d_6) δ 10.7. ^{13}C NMR (acetone-d_6) δ 155.7, 145.2, 139.6, 120.5, 119.5, 113.1, 69.0,

35.6, 32.4, 30.4, 30.2, 27.0, 23.4, 14.4. ^{1}H NMR (acetone-d_6) δ 7.03, 6.68, 3.95, 1.84, 1.54, 1.37, 1.30, 0.92. Anal. calcd. for $C_{96}H_{150}N_3P_3O_{12}$: C, 70.69; H, 9.27; N, 2.58. Found: C, 67.54; H, 9.03; N, 2.70. Similar procedures were followed using 1-chloropentane and 1-iodopentane. Reaction times for 1-chloropentane and 1-iodopentane with **2** were 3 weeks and 5 days, respectively. A pale yellow solid was obtained after purification [yield 36% (chloride) and 62% (iodide)]. The NMR data of the product for these two reactions were identical. Hexa-[3-*tert*-butyl-4-*n*-pentanoxyphenoxy]-cyclotriphosphazene (**6**): ^{31}P NMR (toluene-d_8) δ 11.09. ^{13}C NMR (toluene-d_8) δ 155.4, 145.6, 139.4, 121.0, 119.6, 112.8, 68.5, 35.6, 30.4, 30.0, 29.3, 23.2, 14.6. ^{1}H NMR (toluene-d_8) δ 7.39, 7.12, 6.47, 6.44, 3.58, 1.64, 1.41, 1.31, 0.88. Anal. calcd. for $C_{90}H_{138}N_3P_3O_{12}$: C, 69.88; H, 8.99; N, 2.72. Found: C, 69.09; H, 8.94; N, 3.27 and C, 68.57; H, 8.93; N, 3.06.

Reaction of 2 with Adipoyl Chloride to Yield Polymer 7

To a 25 mL flask was added a magnetic stirrer, 1.0 g (0.89 mmol) of **2**, and 10 mL of dry 1,4-dioxane. A condenser with as addition adapter was added, and the apparatus was sealed with septum stopper and flushed with dry nitrogen. To this, 3.87 mL (27 mmol) of adipoyl chloride was added by syringe and the resulting mixture was heated to reflux for 6 h. After cooling, the resulting mixture was added to a 250 mL separatory funnel containing 50 mL of water. The aqueous solution was extracted with three 50 mL portions of diethyl ether. The organic phases were collected and the diethyl ether was stripped using a rotary evaporator to yield a brown solid, polymer **7** (27% yield). Polymer **7**: ^{31}P NMR (acetone-d_6) δ 9.90. ^{13}C NMR (acetone-d_6) δ 174.0, 171.3, 147.4, 146.1, 142.4, 125.2, 119.1, 118.4, 66.5, 65.1, 34.1, 32.9, 27.0. DSC T_m 62°C. TGA T_d 161°C. Dilute Solution LLS M_w (3.3 ± 1.0) × 10^5, root mean square (RMS) radius 152.0 ± 37.5 nm, dn/dc = 0.121 mL/g.

Reaction of 2 with Succinyl Chloride to Yield Polymer 8

To a dry 50 mL flask was added 2.0 g (1.78 mmol) of **2**, 30 mL of dry 1,4-dioxane, and a magnetic stirrer. A condenser with an addition adapter was added and the apparatus was sealed with septum stopper and flushed with dry nitrogen. Succinyl chloride (5.9 mL, 53.5 mmol) was added by syringe and the resulting mixture was heated to reflux for 48 h upon which the excess succinyl chloride was quenched with water and polymer **8** was isolated by extraction with CH_2Cl_2. Removal of the CH_2Cl_2 afforded a tan-colored solid that was purified by extraction of impurities with hot water in a soxhlet extractor to give 0.7 g of polymer **8** (51% yield). Polymer **8**: ^{31}P NMR (acetone-d_6) δ 9.95. ^{13}C NMR (acetone-d_6) δ 173.2, 171.2, 148.1, 146.5, 142.9, 125.4, 119.6, 118.8, 34.6, 28.5. DSC T_m 71°C. TGA T_d 207°C. HPSEC-LLS M_w (3.46 ± 0.03) × 10^5, RMS radius 73.4 ± 0.7, polydispersity (M_w/M_n) 1.39 ± 0.02.

Reaction of 2 with Dodecanedioyl Dichloride to Yield Polymers 9 and 10

Polymers **9** and **10** were synthesized using a similar method. Polymer **9** was synthesized with a ratio of acid chloride/aromatic hydroxyl on phosphazene of 3.5 and for polymer **10** the ratio was 2.0. The representative synthesis of polymer **9** is included here. To a 100 mL flask was added 5.53 g (4.92 mmol) of **2**, 50 mL of dry 1,4-dioxane, a magnetic stirrer, an addition adapter, and a condenser. The system was sealed with septum stopper and purged with dry nitrogen. To this apparatus was added by syringe 12.9 mL (51.6 mmol) of dodecanedioyl dichloride, and the resulting mixture was heated for 22 h and then allowed to cool to room temperature. The excess dichloride was quenched with 1 L of water and the insoluble solids were collected by centrifugation. These solids were then treated with 100 mL of diethyl ether and centrifuged to remove insoluble material. The solution was collected by decantation and polymer **9** was isolated by removal of solvent to give 6.9 g (60% yield) of a tan solid. Polymer **9** and **10**: ^{31}P NMR (acetone-d_6) δ 10.0. ^{13}C NMR (acetone-d_6) δ 174.9, 172.0, 148.2, 146.9, 143.1, 125.9, 119.9, 119.2, 34.9, 34.0, 25.3. Polymer **9**: DSC T_g 14°C, T_1 53°C, T_m 115°C. TGA T_d 207°C. HPSEC LLS M_w (1.39 ± 0.6) × 10^6, RMS radius 103.9 ± 24.9 nm, polydispersity (M_w/M_n) 1.99. Polymer **10**: DSC T_g 21°C, T_1 56°C, T_m 116°C. TGA T_d 201°C. HPSEC LLS M_w (1.22 ± 0.5) × 10^6, RMS Radius 103.4 ± 20.9 nm, polydispersity (M_w/M_n) 3.03. Yield = 41%.

DISCUSSION

Nucleophilic Substitution Chemistry

Syntheses of crosslinked **1**[16] and neat cyclic trimer **2**[17] have been reported to occur in a facile

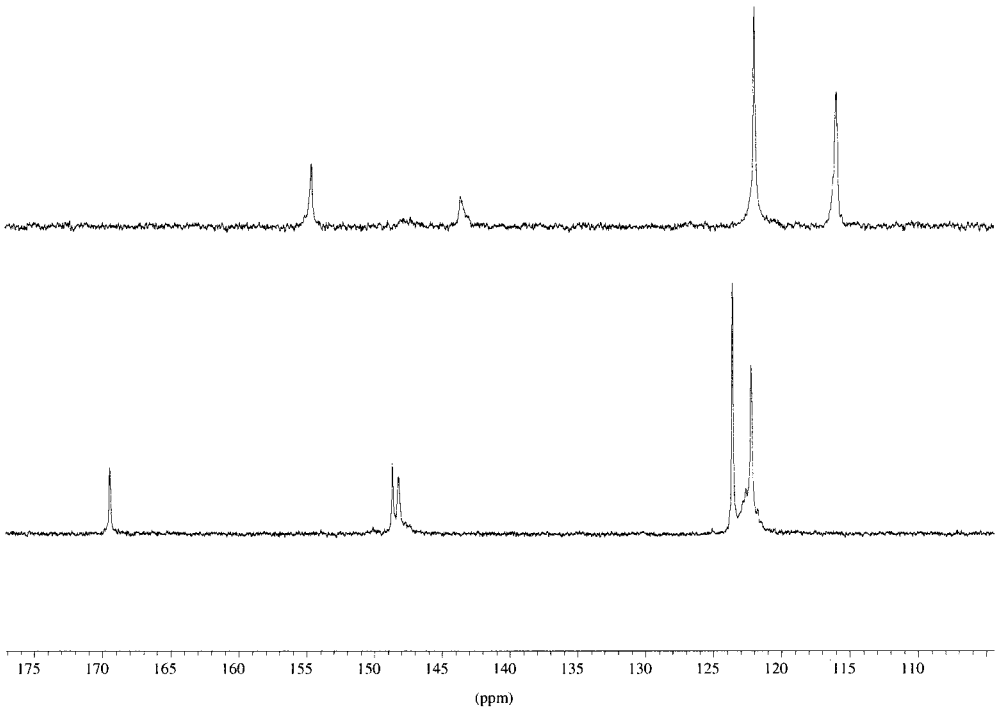


Figure 3 ^{13}C NMR spectra of **1** (top) and acetylated **3** (bottom).

manner with high yields. Each of these cyclotriphosphazenes contains free aromatic hydroxyl groups that afford synthetic pathways to expand the chemistry of these systems. As a probe of the chemistry of these phosphazenes, **1** was allowed to react with acetic anhydride for 2 h in the presence of 4-picoline to yield hexa-[4-acetyloxyphenoxy]cyclotriphosphazene (**3**). This reaction has been successfully performed on uncrosslinked **1** in neat pyridine,[14] yielding a functionalized cyclic trimer. The aromatic region of the ^{13}C NMR spectrum between 115 and 128 ppm provided evidence for the completion of the acetylation reaction (see Fig. 3). Peaks assigned to the protonated aromatic carbons at 122.1 and 123.6 ppm for compound **3** replaced the two analogous peaks for **1** at 115.9 and 121.9 ppm. Additional evidence is provided by the presence of a resonance at 169.4 ppm corresponding to the carbonyl of the acetyloxy group. The ^{31}P NMR spectrum of **3** was unexpected. As discussed earlier, the ^{31}P spectrum of **1** is complex, while the spectrum of **3** revealed only one peak. It is not inferred from this result that the partially crosslinked nature of **1** has been disrupted. To the contrary, it is proposed that the partially crosslinked structure has been maintained and it is coincidental that the separate peaks that would be expected are not resolved at 7.04 T magnetic field strength. This conclusion is supported by thermal analysis, DSC and TGA experiments that showed a clear T_g at 69°C, T_d at 250°C, and no observed melting point. This is in contrast to the uncrosslinked analog of **3** as reported by Gleria and Medici,[14] where a distinct melting point at 179°C was measured.

Hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene (**2**) was of interest for further chemical modification (see Fig. 4), due to the *tert*-butyl group, which increases the solubility of **2** in common solvents as compared to compound **1**. Furthermore, **2** is generally synthesized and isolated in greater yield than **1**. Acetylation of **2** could be followed by ^{13}C NMR spectroscopy. Three resonances (see Fig. 5) were noted for **2** between 115 and 128 ppm that correspond to the protonated aromatic carbons: 116.0, 118.1, and 119.0 ppm. In the spectrum obtained for compound **4**, the protonated aromatic carbons (carbons 2, 5, and 6; see Fig. 2) were shifted to 117.2, 119.3, and 126.1 ppm, respectively, indicating complete acetylation. Additionally, the expected carbonyl resonance, located at 169.4 ppm, was observed. Thermal characterization revealed a T_g at 65°C and a T_d of 370°C. Interestingly, no clear melting point is observed by either optical melting point determination or by DSC, in contrast to

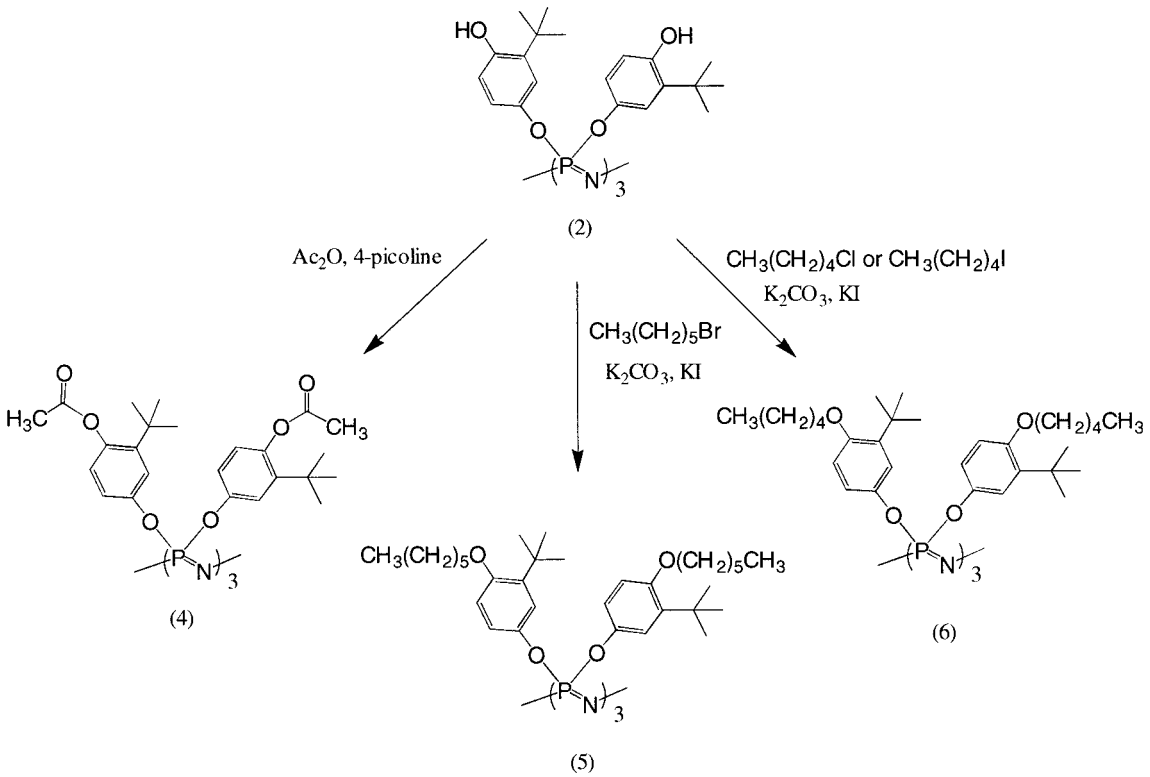


Figure 4 Reaction chemistry of hexa-[3-*tert*-butyl-4-hydroxyphenoxy]cyclotriphosphazene (**2**).

the observed behaviors of related neat cyclic trimers (without *tert*-butyl groups attached to the aromatic rings).[14]

The chemistry of **2** was probed under milder conditions through the reaction with alkyl halides with catalytic amounts of K_2CO_3 and KI. Reactions with 1-bromohexane in acetone generally required five days at reflux to obtain total conversion of **2** to hexa-[3-*tert*-butyl-4-*n*-hexanoxyphenoxy]cyclotriphosphazene (**5**). The most significant feature in the ^{13}C NMR spectrum was the resonance assigned to carbon 4 observed at 155.7 ppm for **5** as compared to 152.4 ppm for **2**, indicating functionalization of the free hydroxyl. It is proposed that this reaction proceeds through deprotonation of the hydroxyl followed by nucleophilic attack on the alkyl halide wherein the halide is displaced. To support this hypothesis and to further diversify the chemistry of this phosphazene, analogous reactions with 1-iodopentane and 1-chloropentane were conducted. Reaction with 1-iodopentane required five days at reflux for complete reaction, similar to that of 1-bromohexane. However, 1-chloropentane required significantly longer, up to three weeks, to complete. It is proposed that the difference between the chloroalkane reaction and the bromo/iodoalkane reactions is due to leaving group effects. These data fully support an S_N2 mechanism for this substitution reaction.

Polymerization Chemistry

Given the reactivity of **2** toward an acid anhydride, polymerization products should reasonably be expected using bifunctional organic linkers such as diacid chlorides. Ideally, a reaction between a poly-hydroxylated cyclotriphosphazene and a diacid chloride would yield an cyclomatrix phosphazene polyester. An increased degree of confidence in this concept was provided by a recent paper where the authors reported successful polymerizations using an acid chloride functionalized cyclotriphosphazene and the diol bisphenol A.[22]

Reactions were conducted with a threefold excess of adipoyl chloride under refluxing conditions and were monitored by ^{13}C NMR spectroscopy.

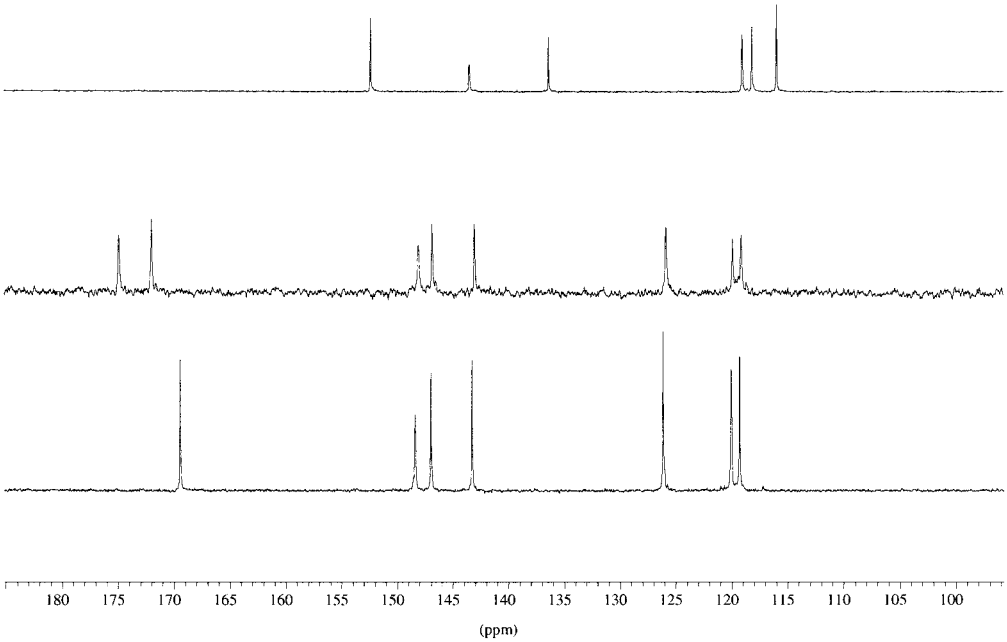


Figure 5 ^{13}C NMR spectra of the aromatic region for **2** (top), **4** (bottom), and polymer **9** (middle). The spectra were collected at room temperature in acetone-d_6 as the solvent.

The aromatic region between 128 and 115 ppm showed a very similar fingerprint to the acetylation reactions, but the aliphatic region was dominated by six large peaks that could not be attributed to either the adipoyl chloride or **2**. Vacuum distillation of the products of this reaction revealed a copious amount of a high boiling clear viscous oil. Characterization of the oil by carbon and proton two-dimensional NMR experiments revealed it to be an adipoyl chloride adduct to ring-opened THF (see Fig. 6). Ring opening of THF was a curious side product of this synthetic reaction; however, this is not a new phenomenon. Cleavage of ethers by acid chlorides in the presence of cobalt (II) catalysts has been studied.[23] Without a rigorous investigation, it is not possible to propose a detailed mechanism except to assert that the cyclotriphosphazene may act as a catalyst for the formation of the THF adduct.

To eliminate the unwanted side product, THF was replaced by 1,4-dioxane, which is known to be more resistant to ring-opening chemistry. In this solvent, Polymer **7** was synthesized as a brown glass-like solid. High solubility in THF and chloroform afforded detailed liquid state ^{13}C NMR analysis of polymer **7**. The observed shift of the protonated aromatic carbons was consistent with acetylated product (**4**). Additionally, two peaks at 174.0 and 171.3 ppm were noted. From analogy to the acetylation reactions, the peak at 171.3 ppm was assigned to the ester carbonyl and the peak at 174.0 ppm was assigned to an free acid functionality (COOH). The data suggest that attachment of adipoyl chloride occurs both in a bidentate pathway forming a crosslink between two cyclotriphosphazene rings and in a monodentate fashion wherein one end of the diacid chloride attaches to the phosphazene and the other end is hydrolyzed during product purification. Spectral deconvolution of carbonyl peaks revealed that they have approximately equal area suggesting that the average mer contains has three monodentate pendant groups and three crosslinking pendant groups.

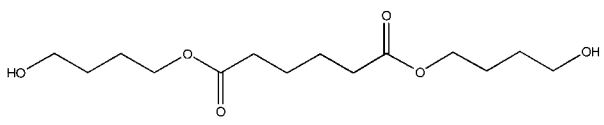


Figure 6 Proposed structure of the oil formed during the reaction of **2** with adipoyl chloride in THF.

LLS was employed to determine the M_w for Polymer **7**, measured at 330,000 daltons suggesting a high degree of bidentate linkages between cyclotriphosphazene rings (see Table I). Using the ^{13}C NMR carbonyl peak areas, an estimation of the average number of mers per chain was calcu-

Table I Thermal and Molecular Weight Characterization Data for Polymers 7–10

Polymer	M_w ($\times 10^5$ g/mol)	M_w/M_n	T_g (°C)	T_1 (°C)	T_m (°C)	T_d (°C)
7	3.3 ± 1.0	—	None observed	61	None observed	161
8	3.46 ± 0.03	1.39	None observed	71	None observed	207
9	13.9 ± 6	1.99	14	53	115	207
10	12.2 ± 5	3.03	21	56	116	201

lated at 247. This was accomplished by using the relative peak areas to estimate the percentages of both mono- and bidentate pendant groups on an average cyclotriphosphazene ring. From this, an average molecular weight per mer was calculated; thus the estimated number of mers is equal to the M_w divided by the mer molecular mass. Thermal analysis of polymer **7** showed only a T_1 endotherm at 61°C and that onset of thermal decomposition begins at 161°C. The most notable feature of this new polymer is the high degree of solubility in organic solvents, a property that is not common for cyclomatrix phosphazenes.

An investigation into shorter chain length bridges was investigated using succinyl dichloride. The reaction time was 48 h and the product, polymer **8**, was isolated as a tan-colored brittle glassy solid. Thermal analysis indicated a T_1 endotherm at 71°C and decomposition weight loss beginning at 207°C. Similar to polymer **7,** ^{13}C NMR spectra data showed the same general trend with three peaks for the protonated aromatic carbons at positions 2, 5, and 6, and two peaks in the carbonyl region (ester and acid). Molecular weight characterization of this polymer was accomplished through HPSEC with LLS detection (see Table I). The degree of polymerization was similar that of polymer **7** with approximately 191 mers per chain as estimated from the ^{13}C NMR spectrum.

Reactions with dodecanedioyl dichloride were observed to give waxy polymeric products, polymers **9** and **10**, with the waxy nature of the products attributed to the increased aliphatic carbon content of the diacid. These polymerizations were performed at three different stoichiometries to investigate the effect that the synthetic process has on molecular weight. Ratios of diacid chloride to aromatic hydroxyl studied included 1.0:1, 2.0:1, and 3.5:1. At ratios of 2.0:1 and 3.5:1, soluble polymers were isolated and characterized. Figure 5 contains a plot of the aromatic and carbonyl region for polymer **9** which illustrates the significant resonances in the ^{13}C NMR spectra, including both carbonyl peaks. Molecular weights (M_w) for these species were measured in the 10^6 range and confirmed the polymeric nature of the products. Additionally, through deconvolution of the carbonyl resonances in the ^{13}C NMR spectra, the average number of mers per polymer chain was estimated at 826 and 678 for polymers **9** and **10**, respectively. The degree of polymerization in polymers **9** and **10** are clearly higher than for the shorter chain crosslinkers by a factor of three. A potential explanation for this behavior is that the longer crosslinkers allow the phosphazene rings to be distant as compared the shorter chain systems, thus minimizing steric encumbrance and encouraging a higher degree of polymerization.

A ratio of 1.0:1 was investigated. The reaction solution solidified during reflux forming a 1,4-dioxane-swollen gel. Attempts to isolate soluble polymer through removal of the solvent under reduced pressure followed by dissolution in other solvents were performed without success. It is proposed that this material was highly crosslinked. To control the amount of bidentate reactivity, an excess of diacid chloride is necessary to occupy the hydroxyl sites in a monodentate fashion, thus reducing the number of crosslinks.

Thermal analytical data of polymers **9** and **10** were similar to each other, as expected. The significant difference between the polymer data observed for the shorter chain systems and for polymers **9** and **10** was a measurable T_g. The T_g for polymers **9** and **10** was 14 and 21°C, respectively. Additionally, two T_1 endotherms were observed, similar to polymers **7** and **8**. Onset of decomposition (T_d) for both of these polymers was measured in excess of 200°C.

CONCLUSION

New cyclomatrix phosphazene polymers were synthesized from the reaction between bifunc-

tional acid chlorides and **2**, a hydroxylated cyclotriphosphazene. Acid chlorides, both mono- and bidentate, were found to readily react with the hindered hydroxyl of **2**, consistent with data reported in the literature for **1**.

The use of bidentate organic acid chlorides led to the synthesis of cyclomatrix polymers. Materials synthesized in this work were formed using three different chain lengths of organic crosslinker. The shorter crosslinkers generally formed polymers that were glassy and fully soluble in solvents such as THF and acetone. The longer aliphatic C_{12} chain imparted a waxy character onto the polymer that was an embodiment of the physical properties of this longer component.

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