Synthesis and Characterization of Poly{hexakis[(methyl)(4-hydroxyphenoxy)]cyclotriphosphazene}

THOMAS A. LUTHER, FREDERICK F. STEWART, ROBERT P. LASH, JOHN E. WEY, MASON K. HARRUP

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

Received 27 October 2000; accepted 14 February 2001

ABSTRACT: The reaction of methylhydroquinone with hexachlorocyclotriphosphazene in the presence of a base, 4-picoline, in cyclohexane was investigated. Nuclear magnetic resonance spectroscopy, multiangle laser light scattering, and elemental analyses were performed on the product and two other related phosphazene materials produced by analogous synthetic routes: poly[hexakis(4-hydroxyphenoxy)cyclotriphosphazene] **(1)** and hexakis[(3-*tert*-butyl)(4-hydroxyphenoxy)]cyclotriphosphazene **(2)**. Unlike the data for **2** where the *tert*-butyl moiety enforced regiospecific nucleophilic addition, the data for the methylhydroquinone-substituted cyclotriphosphazene product indicate that the less sterically bulky methyl group provides only limited protection for the adjacent hydroxyl group. The result is the formation of a low molecular weight oligomer, poly{hexakis[(methyl)(4-hydroxyphenoxy)]cyclotriphosphazene} **(3)**, instead of a discrete cyclic trimer species.
 J Appl Polym Sci 82: 3439–3446, 2001

Key words: phosphazenes; polymers; cyclomatrix; cyclotriphosphazene; methylhydroquinone

INTRODUCTION

Polyphosphazenes have been shown to have a wide range of thermal and chemical stabilities.[1,2] Depending on the type of pendant groups that are utilized, this breadth of thermal and chemical stability has enabled polyphosphazenes to have an extensive range of applications.[3–6] Linear polyphosphazenes have been the most extensively researched polyphosphazene material (Fig. 1).[7,8] Linear polyphosphazenes are generally synthesized by ring-opening polymerization of hexachlorocyclotriphosphazene followed by the addition of organic nucleophiles to the backbone.[9] The relative ease of synthetic adaptation of linear polyphosphazenes with the desired characteristics has been the driving force for developing these materials. Due to the high cost of materials and relatively low yields resulting from the ring-opening polymerization reaction of hexachlorocyclotriphosphazene, other routes to polyphosphazene materials are being investigated. Included are methods for the production of linear polyphosphazenes that involve the synthesis of linear materials from nitrogen- and phosphorus-containing precursors directly.[10–12]

There are two other backbone configurations for polyphosphazenes based upon a cyclotriphosphazene: cyclolinear and cyclomatrix. The complexities involved with the synthesis of cyclolinear materials[13] severely limit their desirability; hence, more research is being focused on the generation of cyclomatrix materials.[7] The general routes to these materials are the addition of bifunctional organic nucleophiles to hexachlorocyclotriphosphazene followed by crosslinking or the

Correspondence to: T. A. Luther.
Contract grant sponsor: U.S. Department of Energy; contract grant number: DE-AC07-99ID13727.

Journal of Applied Polymer Science, Vol. 82, 3439–3446 (2001)

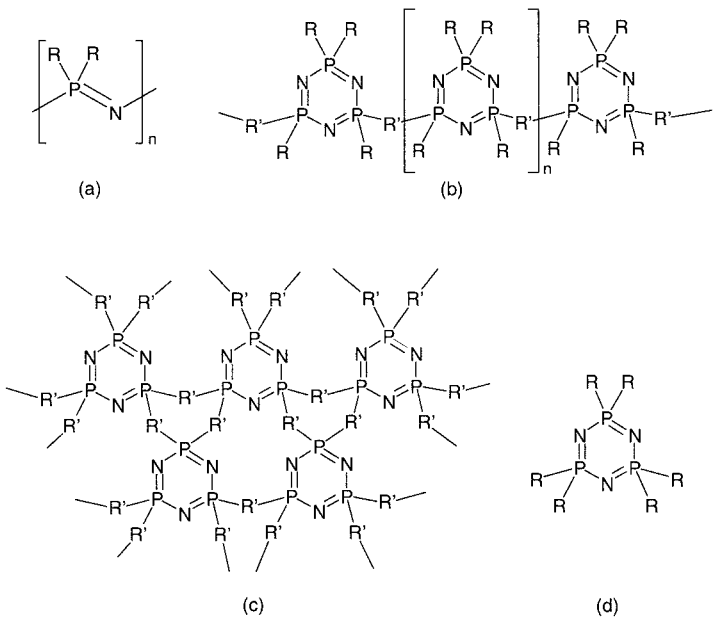


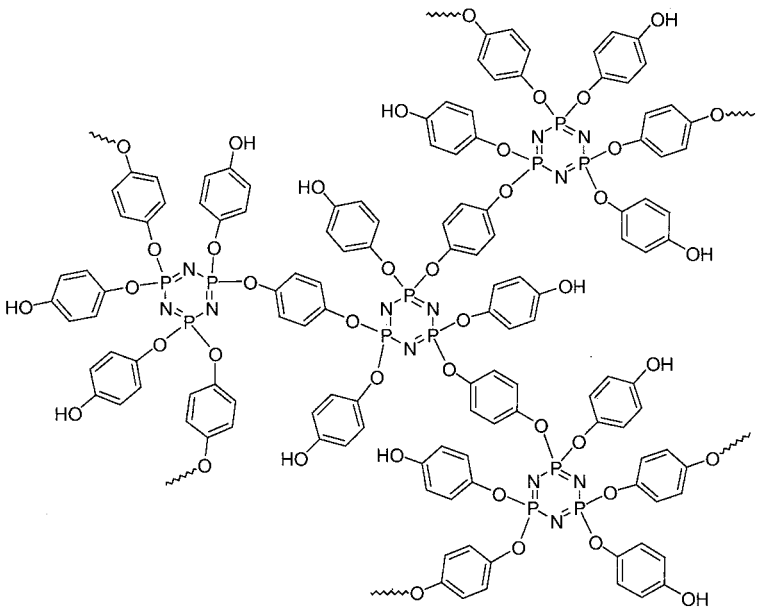
Figure 1 Backbone configurations of polyphosphazenes: (a) linear; (b) cyclolinear; (c) cyclomatrix; (d) cyclotriphosphazene. R and R′ represent monodentate and bidentate pendant groups, respectively.

initial addition of nucleophiles with functional groups that can be further substituted or modified prior to crosslinking.

Earlier work exploring the generation of polymer precursors reported the synthesis and characterization of poly[hexakis(4-hydroxyphenoxy)cyclotriphosphazene] **(1)** by a one-step nucleophilic substitution method.[14,15] Hexachlorocyclotriphosphazene was reacted with hydroquinone in cyclohexane with pyridine as a base to absorb the HCl generated by the reaction.[15] Elemental analysis and ^{31}P-NMR spectroscopy determined the product to be a crosslinked polymer instead of a distinct cyclic trimer (Fig. 2). Polymerization is due to the presence of two unprotected hydroxyl functional groups on hydroquinone. Even a large excess of hydroquinone does not completely obviate the nucleophilic attack at both hydroxyl sites. The synthesis of hexakis(4-hydroxyphenoxy)cyclotriphosphazene as a discrete cyclic trimer has been accomplished through a two-step process by reacting hexachlorocyclotriphosphazene with either 4-methoxyphenol or 4-(benzyloxy)phenol to form the phosphonitrilic complexes hexakis(4-methoxyphenoxy)cyclotriphosphazene[16] or hexakis[4-(benzyloxy)phenoxy]cyclotriphosphazene.[17] The deprotection of the methyl or benzyl residues to hydroxyl moieties results in the generation of the cyclic trimer, hexakis(4-hydroxyphenoxy)cyclotriphosphazene.[17]

Hexakis[(3-*tert*-butyl)(4-hydroxyphenoxy)]cyclotriphosphazene (**2**) (Fig. 3) was synthesized by reacting hexachlorocyclotriphosphazene with *tert*-butylhydroquinone via the one-step nucleophilic substitution method used earlier for the formation of **1**.[18] The bulky nature of the *tert*-butyl group adjacent to one of the hydroxyl groups effectively provides enough steric hindrance that only the nonhindered hydroxyl site is available for the reaction with hexachlorocyclotriphosphazene. The result is a regiospecific substitution reaction with only discrete cyclic trimers being produced.

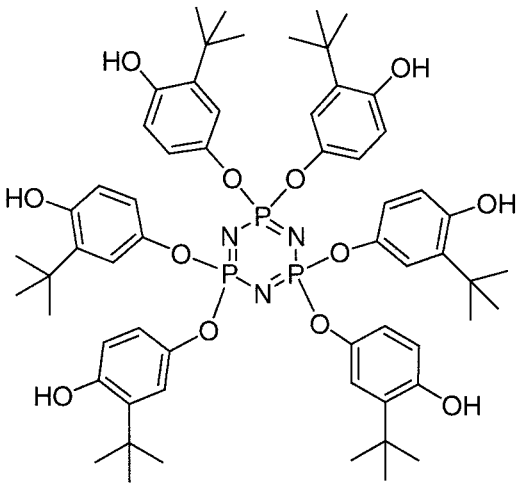
A recent study reported the preparation of cyclomatrix materials utilizing **1** and **2** as precursors.[19] The steric hindrance associated with the *tert*-butyl group adjacent to the reactive hydroxyl site resulted in longer reaction times for the addition of organic crosslinkers to **2** compared to the reaction times with **1**. The formation of **2** as a single species by the one-step nucleophilic substitution method and the subsequent reactions forming cyclomatrix materials stimulated interest in further studies to generate cyclic trimers that have sites of differing reactivities for additional modification. Methylhydroquinone was chosen in this study to explore its potential as a cyclomatrix precursor due to the reactivity of benzylic methyl groups. If the substitution reaction with hexachlorocyclotriphosphazene via the one-step method occurs in a regiospecific manner,



1

Figure 2 Poly[hexakis(4-hydroxyphenoxy)cyclotriphosphazene] **(1)**.

forming a cyclic trimer, the product could be further modified at either the methyl or the hydroxyl positions. The relative ease of substitution at the available hydroxyl position and the ability to further tune desired physical properties into the final product by modification at the reactive methyl site would give this cyclomatrix precursor a distinct synthetic advantage over **2**. The synthesis and characterization of poly{hexakis[(methyl)(4-hydroxyphenoxy)]cyclotriphosphazene} **(3)**, a low molecular weight oligomer, is reported here along with molecular weight and elemental analyses of the related cyclotriphosphazene materials **1** and **2**.



2

Figure 3 Hexakis[(3-*tert*-butyl)(4-hydroxyphenoxy)]cyclotriphosphazene **(2).**

EXPERIMENTAL

General

NMR data were acquired on a Bruker DMX 300WB spectrometer operating at 300.13 MHz (^{1}H), 121.49 MHz (^{31}P), or 75.78 MHz (^{13}C) and referenced internally to TMS (^{1}H and ^{13}C) or externally to H_3PO_4 (^{31}P). The materials for study by NMR spectroscopy were prepared as dilute solutions using acetone-d_6 (Cambridge Isotope Laboratories, Andover, MA) as the solvent. Hexachlorocyclotriphosphazene (Strem Chemicals, Inc., Newburyport, MA) was purified by sublimation prior to use. Methylhydroquinone, 4-picoline, and HPLC-grade tetrahydrofuran (Aldrich Chemical Co., Milwaukee, WI) were used as received. Cyclohexane (Aldrich Chemical Co.) was distilled over calcium chloride prior to use. Toluene (Al-

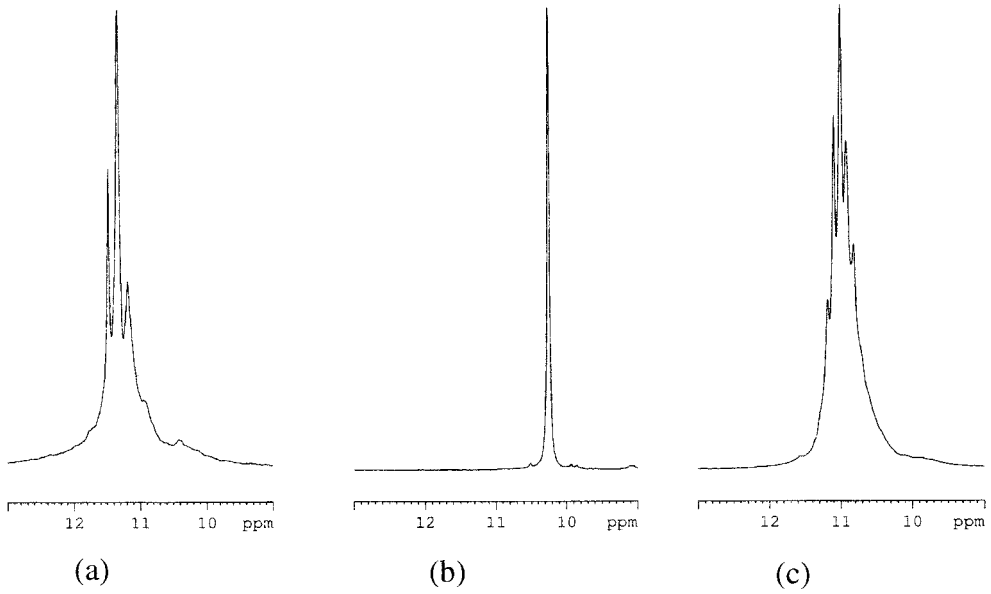


Figure 4 ^{31}P-NMR spectra (in acetone-d_6) of (a) poly[hexakis(4-hydroxyphenoxy)cyclotriphosphazene] **(1)**, (b) hexakis[(3-tert-butyl)(4-hydroxyphenoxy)]cyclotriphosphazene **(2)**, and (c) poly{hexakis[(methyl)(4-hydroxyphenoxy)]cyclotriphosphazene} **(3)**.

drich Chemical Co.) was distilled prior to use. Elemental analyses (C, H, and N) were performed on a Carlo Erba Instruments EA1108 CHNS-O elemental analyzer.

Characterization of Molecular Weights

Dilute solution techniques were used to characterize the macromolecular structures of the cyclic trimers/polymers. Tetrahydrofuran, filtered through a 0.02-μm Whatman Anatop™ 25 syringe filter, was used as the 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 detector 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 which uses polarized light (633 nm) to measure scattered light intensities at 18 angles ranging from 22.5° to 147°. The instrument was calibrated with toluene, which was filtered through a 0.02-μm filter. Zimm and Debye plots were prepared to obtain weight-average molecular weights, z-average square radii (mean square radii), and second virial coefficients.

Synthesis of Poly[hexakis(4-hydroxyphenoxy)cyclotriphosphazene] (1)

Poly[hexakis(4-hydroxyphenoxy)cyclotriphosphazene] **(1)** was prepared as previously reported.[15] $M_w = (4.52 \pm 0.09) \times 10^5$ g/mol, $dn/dc = 0.143$, RMS radius = 56.5 ± 1.7 nm, second virial coefficient = $(-3.54 \pm 0.3) \times 10^{-4}$ mol mL/g^2.

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

Hexakis[(3-*tert*-butyl)(4-hydroxyphenoxy)]cyclotriphosphazene **(2)** was prepared as previously reported.[18] $M_w = (1.07 \pm 0.1) \times 10^3$ g/mol, $dn/dc = 0.138$, RMS radius < 10 nm, second virial coefficient = $(2.82 \pm 3.0) \times 10^{-3}$ mol mL/g^2.

ANAL. Calcd for $C_{60}H_{78}N_3O_{12}P_3$: C, = 63.99%; H, = 6.98%; N, = 3.73%. Found: C, = 64.50 ± 0.16%; H, = 7.17 ± 0.04%; N, = 3.79 ± 0.02%.

Synthesis of Poly{hexakis[(methyl)(4-hydroxyphenoxy)]cyclotriphosphazene} (3)

A flame-dried 2-L three-neck round-bottom flask, equipped with a water condenser, mechanical stirrer, and a pressure-equalizing addition funnel, was charged with hexachlorocyclotriphosphazene (23.6 g, 67.9 mmol) and methylhydroquinone

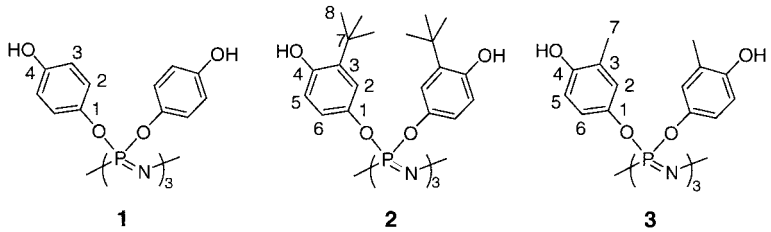


Figure 5 Carbon numbering scheme for the cyclotriphosphazene materials.

(100.6 g, 0.810 mol). Cyclohexane (800 mL) was added and the mixture was stirred while under a flow of nitrogen for 30 min. 4-Picoline (79 mL, 0.81 mol) was slowly added to the reaction mixture (over 10 min) from the addition funnel. The reaction mixture was then heated at reflux for an additional 16 h. During the heating process, a colorless clear upper layer and an orange viscous lower layer were observed. After the reaction mixture was cooled to room temperature, the clear colorless liquid was decanted from the orange solid. Aqueous acetic acid (80%, 500 mL) was added to the orange solid followed by mild heating and stirring until the solid completely dissolved, resulting in a clear orange solution. The acidic solution was poured into 3 L of room-temperature deionized water, resulting in the formation of an off-white precipitate. The precipitate was collected by suction filtration, transferred to a cellulose Soxhlet thimble, and extracted with water for 4 days. Upon drying under vacuum, 36.3 g of **3** was obtained in a 61% yield.

^{31}P-NMR (acetone-d_6) δ 11.0 (m). ^{13}C{^{1}H}-NMR (acetone-d_6) δ 154.9, 153.2, 144.4, 143.3, 131.9, 126.0, 123.9, 122.1, 119.6, 118.2, 115.7, 113.8, 16.9, 16.3. ^{1}H-NMR (acetone-d_6) δ 8.19, 6.79–6.48 (m), 2.13, 1.98. M_w = (4.98 $\pm$ 0.06) $\times$ 10^3 g/mol, dn/dc = 0.150, RMS radius $<$ 10 nm, second virial coefficient = (1.58 $\pm$ 0.6) $\times$ 10^{-4} mol mL/g^2.

ANAL. Calcd for $C_{42}H_{42}N_3O_{12}P_3$: C, = 57.7%; H, = 4.85%; N, = 4.81%. Found: C, = 56.0 $\pm$ 0.1%; H, = 4.44 $\pm$ 0.12%; N, = 5.37 $\pm$ 0.02%.

RESULTS AND DISCUSSION

The product of the one-step reaction of methylhydroquinone and hexachlorocyclotriphosphazene was studied by NMR spectroscopy, multiangle LLS, and elemental analysis. The complex nature of the observed resonance in the ^{31}P-NMR spectrum of **3** [Fig. 4(c)] is consistent with the addition of the methylhydroquinone occurring in a nonregiospecific manner with respect to the hexachlorocyclotriphosphazene. Since there are two hydroxyl groups on the methylhydroquinone that could react with the phosphorus-bound chlorines, substitution could occur at either position. Although the preferred substitution site is at the less hindered position, the ^{31}P-NMR analysis strongly suggests that the methyl group does not provide full protection for the adjacent hydroxyl group. This nonregiospecific directing force leads to both 3-methyl and 2-methyl substitution patterns on the phosphazene rings. To further complicate the speciation, some degree of crosslinking is also to be expected with a mixture of substitution patterns.

The ^{13}C{^{1}H}-NMR spectrum of **3** exhibits six major resonances for the aromatic carbons that are analogous with the NMR spectra reported for the aromatic carbons in **1** and **2** (Fig. 5 and Table I). The other observable major resonance is assigned to the benzylic methyl carbon upfield from the aromatic carbons at δ = 16.3. The interpretation of the ^{31}P-NMR spectrum that nonregiospecific addition of the methylhydroquinone in the

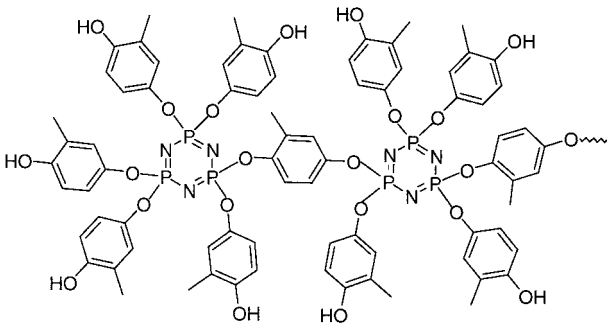
Table I ^{13}C-NMR Chemical Shifts for the Cyclic Phosphazene Materials

			3	
Carbon No.	**1** (ppm)	**2** (ppm)	Major (ppm)	Minor (ppm)
1	144.3	143.5	144.4	143.3
2	122.7	119.0	123.9	122.1
3	116.7	136.4	126.0	131.9
4	155.4	152.4	153.2	154.9
5		118.1	119.6	118.2
6		116.0	115.7	113.8
7		34.1	16.3	16.9
8		28.7		

Table II Molecular Weight of the Cyclic Phosphazene Materials

Structure	M_w (g/mol) Calculated[a]	M_w (g/mol) Determined
1	790	452,000 ± 9000
2	1126	1070 ± 100
3	874	4970 ± 60

[a] Molecular weight calculated for a discrete cyclic trimer.



3

Figure 6 Poly{hexakis[(methyl)(4-hydroxyphenoxy)] cyclotriphosphazene} **(3).**

formation of **3** occurs is supported by the observation of minor resonances that are slightly shifted from the major resonances. Integration of the methyl resonances in the ^{13}C-NMR spectrum (without ^{1}H decoupling) indicates that the minor resonance of the methyl carbon signal represents approximately 17% of the total area of the two signals.

The ^{1}H-NMR spectrum of **3** shows an overlapping multiplet centered at 6.64 ppm for the aromatic protons. The observable major resonances for the hydroxyl and the methyl protons are at 8.19 and 2.13 ppm, respectively. Integration of a minor methyl resonance that is observed slightly upfield ($\delta = 1.98$) from the major methyl resonance agrees with the integration of the methyl resonances in the ^{13}C-NMR spectrum. These data provide further evidence that the methyl group affords only limited protection for the adjacent hydroxyl position, resulting in an 83/17 mixture between 3-methyl and 2-methyl substitution.

The molecular weight of **3** determined by batch-mode multiangle LLS was found to be six times larger than was the calculated weight for the cyclic trimer (Table II). Calculating the degree of oligomerization based upon the molecular weight yields an oligomer comprising approximately six monomer units. This structural unit roughly consists of 4.33 nonbridging to every 1.67 bridging methylhydroquinone moieties and has a chemical composition of 56.4% C, 4.62% H, and 5.46% N. Elemental analysis was also performed on **3** and the results are displayed in Table III. The actual analysis values are more consistent with the theoretical values for the oligomer unit proposed based on LLS measurements than those for a discrete cyclic trimer species. Interpretation of these results yields a basic unit that is a low molecular weight oligomer with one to two bridging methylhydroquinone units per subunit (Fig. 6).

Previously reported NMR data for **1** and **2**, along with molecular weight and elemental analyses that were conducted in this study, were examined to corroborate the proposed structure of **3**. The complex nature of the resonance in the ^{31}P-NMR spectrum for **1** [Fig. 4(a)] is similar to that found for **3** and provides evidence of the presence of both bridging and nonbridging methylhydroquinone moieties. In contrast to **3** and **1**, the formation of **2** occurs with regiospecificity where the

Table III Elemental Analyses of the Cyclic Phosphazene Materials

	1		**2**		**3**	
Element	Calculated[a]	Found	Calculated[a]	Found	Calculated[a]	Found
C%	54.8	50.1	64.0	64.5	57.7	56.0
H%	3.83	3.55	6.98	7.17	4.85	4.44
N%	5.32	6.54	3.73	3.79	4.81	5.37

[a] Chemical composition calculated for discrete cyclic trimers.

tert-butyl group enforces the orientation away from the phosphorus–nitrogen ring during the addition and effectively protects the remaining hydroxyl group from further reaction.[18] This results in the formation of a distinct cyclotriphosphazene with a single resonance in the ^{31}P-NMR spectrum with a half-height full-width line width of less than 4 Hz [Fig. 4(b)].

Comparisons of the molecular weights of **1** and **2** reveal the differences in the effectiveness of the adjacent protecting group in these materials (Table II). The molecular weight of **2** agrees with the calculated value of the cyclic trimer, indicating that the *tert*-butyl group does provide effective protection for the adjacent hydroxyl site during the substitution reaction, thus preventing oligomerization. However, the molecular weight of **1** is almost 3 orders of magnitude larger than is the calculated molecular weight of the cyclic trimer. This high molecular weight agrees with the NMR data that the initial substitution at the first hydroxyl position does not prevent further substitution at the second hydroxyl site, resulting in a significant amount of polymerization.

The elemental analyses of **1** and **2** (Table III) agree with the molecular weight data, confirming the degree of polymerization that occurs in these materials. The authors for **1** reported that using a structural subunit of three nonbridging and three bridging hydroquinone moieties and one water molecule per subunit resulted in a chemical composition that closely matched the elemental analysis of **1**.[15] This structural subunit indicates that half of every monomer unit is involved with crosslinking, resulting in a fairly large amount of polymerization. The elemental analysis of **2** closely matches the calculated chemical composition for the structural formation of a cyclic trimer with no polymerization.

The data for **3** indicate that the existence of a small protecting group such as methyl hinders the substitution reaction. This results in a mixture of 3-methyl and 2-methyl moieties with a limited amount of crosslinking. The NMR, LLS, and elemental analysis data for **1** and **2** further support the interpretation that **3** is best described as a low molecular weight oligomer.

CONCLUSIONS

Utilizing the previously reported one-step reaction method forming the distinct cyclic trimer **2**, methylhydroquinone was reacted with hexachlorocyclotriphosphazene to develop a potential precursor for new cyclomatrix materials. The NMR data for **3** indicate that during the substitution reaction the addition of methylhydroquinone does not occur regiospecifically, resulting in an 83/17 mixture of 3-methyl and 2-methyl moieties. As a consequence of the mixture, a limited extent of oligomerization is observed as shown by elemental analysis and molecular weight data forming a low molecular weight oligomer, **3**, instead of a discrete cyclic trimer.

The oligomerization present in **3** does not necessarily preclude its use as a precursor for the preparation of cyclomatrix materials. The presence of the benzylic methyl group in **3** provides two routes for further substitution or modification. The relatively smaller methyl group allows the use of reactants with larger functional groups in substitution reactions at the hydroxyl position or modification reactions could focus directly on the reactive benzylic methyl group. These differences signify a synthetic advantage for **3** over the sterically bulky *tert*-butyl group in **2** in generating cyclomatrix materials. Further research is currently exploring the preparation of cyclomatrix materials utilizing **3** and related species as precursors.

REFERENCES

1. Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; Laliberte, B. R.; Sacher, R. E.; Matton, R. W. J Polym Sci 1974, 12, 433.
2. Golemme, G.; Drioli, E. J Inorg Organomet Polym 1996, 6, 341.
3. Kumar, D.; Fohlen, G. M.; Parker, J. A. Macromolecules 1983, 16, 1250.
4. Singler, R. E.; Deome, A. J.; Dunn, D. A.; Bieber, M. J. Ind Eng Chem Prod Res Dev 1986, 25, 46.
5. Blonsky, P. M.; Shriver, D. F.; Austin, P.; Allcock, H. R. J Am Chem Soc 1984, 106, 6854.
6. Selvaraj, I. I.; Charklanobis, S.; Chandrasekhar, V. J Electrochem Soc 1995, 142, 3434.
7. De Jaeger, R.; Gleria, M. Prog Polym Sci 1998, 23, 179.
8. Neilson, R. H.; Wisian-Neilson, P. Chem Rev 1988, 88, 541.
9. Mark, J. E.; Allcock, H. R.; West, R. Inorganic Polymers; Prentice-Hall, Englewood Cliffs, NJ, 1992; pp 61–140.
10. Wisian-Neilson, P.; Neilson, R. H. J Am Chem Soc 1980, 102, 2848.

11. Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. Macromolecules 1987, 20, 910.
12. Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. J Am Chem Soc 1995, 117, 7035.
13. For a recent example, see Kellam, E. C., III; Hofmann, M. A.; Allcock, H. R. Am Chem Soc Polym Prepr 2000, 41, 1233.
14. Rice, R. G.; Geib, B. H.; Kaplan, L. A. U.S. Patent 3 121 704, 1964.
15. Femec, D. A.; McCaffrey, R. R. J Appl Polym Sci 1994, 52, 501.
16. Allcock, H. R. Phosphorus–Nitrogen Compounds; Academic: New York, 1972; p 429.
17. Medici, A.; Fantin, G.; Pedrini, P.; Gleria, M.; Minto, F. Macromolecules 1992, 25, 2569.
18. Stewart, F. F.; Harrup, M. K. J Appl Polym Sci 1999, 72, 1085.
19. Stewart, F. F.; Luther, T. A.; Harrup, M. K.; Lash, R. P. J Appl Polym Sci 2001, 80, 242.