A New Route to the Phosphazene Polymerization Precursors, $Cl_3P{=}NSiMe_3$ and $(NPCl_2)_3$

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An improved synthesis of the phosphazene polymerization precursors, hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**), and $Cl_3P{=}NSiMe_3$ (**2**) is reported. The addition of PCl_5 to $N(SiMe_3)_3$ in methylene chloride at 40 °C produced a mixture of phosphazenes which contained 76% of **1**. However, the addition of $N(SiMe_3)_3$ to PCl_5 in methylene chloride at 0 °C, followed by the addition of hexane, provided **2** in 40% yield. The mechanism of the reaction is discussed.

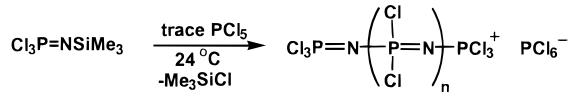
Introduction

Polyphosphazenes form one of the largest classes of inorganic−organic macromolecules.[1] The ease with which these polymers are synthesized has allowed the preparation of several hundred different structures. The simplest route to stable polyphosphazenes is via the replacement of the chlorine atoms in poly(dichlorophosphazene) by a wide variety of organic or organometallic substituents. Different side groups generate different property combinations, hence the selection of appropriate side groups allows the polymer solution properties and materials characteristics to be tailored easily. Various polyphosphazenes are being developed as biomaterials, solid polymer electrolytes, fire-resistant polymers, and elastomeric materials.[1−4]

The traditional method for the synthesis of poly(dichlorophosphazene) has been via the molten phase ring-opening polymerization of hexachlorocyclotriphosphazene (**1**), at 210−250 °C.[1] The polymer formed by this process has a high molecular weight ($\sim 1 \times 10^6$), with a broad molecular weight distribution. The most common method for the preparation of **1** has been through the reaction of PCl_5 with NH_4Cl in a high-boiling halogenated solvent, such as chlorobenzene or tetrachloroethane, at 150 °C. The yields of **1** can approach 70−80% under specialized conditions, but a yield of 50% is more typical.[5−7] The need for ultrahigh purity **1** for the polymerization reaction has placed some limits on the widespread use of this process.

An alternative, ambient-temperature synthesis of poly(dichlorophosphazene) has recently been accomplished.[8] A cationic initiator, such as PCl_5, is added to the phosphoranimine monomer $Cl_3P{=}NSiMe_3$ (**2**) to yield medium molecular weight

Scheme 1



(10^5) polymers $(NPCl_2)_n$ (Scheme 1). This "living" cationic polymerization yields polyphosphazenes with narrow molecular weight distributions. Moreover, the molecular weights can be controlled through changes in the monomer-to-initiator ratio. This polymerization has also provided access to well-defined block copolymers and star polymers, both of which were unobtainable before the introduction of this method.[9,10] The new approach also allows the formation of phosphazene−organic block copolymers.

The key requirement for the broad utilization of this process is an improved synthesis of $Cl_3P{=}NSiMe_3$. The method described in published work[8] involves the reaction of PCl_5 with $LiN(SiMe_3)_2$ at −78 °C in hexane. The phosphoranimine was first synthesized from PCl_5 and $LiN(SiMe_3)_2$ by Niecke and Bitter with a yield of 20%.[11] Honeyman, Lough, and Manners improved the yield to 60% by lowering the reaction temperature from +10 to −78 °C.[12] As was mentioned in a previous publication,[8] the synthesis of pure **2** by the literature method is a challenge. The synthesis routinely produces $ClN(SiMe_3)_2$ as a side product, which is not separable from $Cl_3P{=}NSiMe_3$ by distillation. This compound is a powerful inhibitor of the polymerization. The method developed for purification uses the reaction of $ClN(SiMe_3)_2$ with PPh_3 to form $Ph_3P{=}NSiMe_3$ which can easily be separated from the desired monomer **2** by vacuum distillation. The pure, isolated yield of **2** via this process tends to be low (<40%).

Here we report the reaction of $N(SiMe_3)_3$ with phosphorus pentachloride as a route to either hexachlorocyclotriphosphazene (**1**) or the pure phosphoranimine monomer, $Cl_3P{=}NSiMe_3$(**2**). One product or the other can be favored through variations in the reaction conditions.

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Table 1. Results of the Reaction of $N(SiMe_3)_3 + PCl_5$ under Various Conditions

$N(SiMe_3)_3$:PCl_5	solvent	temp (°C)	reaction time	monomer yield[a]	trimer yield[a]	comments
1:1	THF	25	4 h	0%	0%	PCl_5 reacts with THF
2:1	hexane	0	8 h	20%	0%	
1:1	cylcohexane	0	8 h	22%	0%	
1:1	CH_2Cl_2	−78	4 h	<5%	<5%	
2:1	CH_2Cl_2	25	7 h	8%	68%	slow addition
1:1	CH_2Cl_2	25	12 h	0%	49%	fast addition
1.2:1	CH_2Cl_2	25	30 min	57%	36%	fast addition

[a] Yields obtained from ^{31}P NMR integration of reaction mixture.

Results and Discussion

I. General Description of the Method. In an initial attempt to obtain **2** with higher yields in a single step, the interaction of $N(SiMe_3)_3$ with PCl_5 was carried out using the same conditions as those used for the interaction of $LiN(SiMe_3)_2$ with PCl_5 in hexane. This reaction provided a relatively low yield (ca. 20%) of **2** but without the formation of the side product $ClN(SiMe_3)_2$. This avoids one purification step. We then attempted to optimize the yield of this reaction through variations of the reaction conditions such as temperature, solvent, molar ratio of starting materials, and rates of addition of the starting materials.

Side products generated in the formation of **2** include both cyclic and linear oligomeric phosphazenes, which can be removed easily by filtration or distillation. These side products cannot be avoided completely, since it is known from previous work that **2** can react with PCl_5 to form $Cl_3PNPCl_3^+PCl_6^-$. This, in turn, will interact with additional equivalents of **2** to increase the length of the phosphazene chain. At low temperatures, these side reactions are slowed and **2** may be obtained if the reaction products are isolated soon after warming to room temperature. However, relatively high yields of the cyclic trimer, hexachlorocyclotriphosphazene (**1**), were obtained under different conditions. The yields of the cyclic trimer by the $N(SiMe_3)_3 + PCl_5$ route rival those of the well-known $NH_4Cl + PCl_5$ method optimized with catalysts. Some of these results are shown in Table 1. Thus, this new route to $(NPCl_2)_3$ could constitute an alternative to the traditional method which has been used with few variations since 1834.[13,14]

II. Mechanistic Study. To optimize the yield of either **1** or **2**, it was necessary to further understand the mechanism that gives the monomer or the cyclic trimer. The reaction of an equimolar amount of $N(SiMe_3)_3$ and PCl_5 at 25 °C in methylene chloride was chosen for experimentation since the greatest variation in results was obtained under these conditions, as can be seen in Table 1. Crude yields of **2** ranged from 0 to 57%, while the yields of **1** ranged from 5 to 68%.

The reaction was monitored by ^{31}P NMR spectroscopy and the results are shown in Figures 1 and 2. Initially, at the start of the reaction, a significant amount of monomer **2** is formed. The amount of **2** decreases over time, and this compound is eventually consumed. Other compounds identified were $Cl_3PNP(Cl)_2NPCl_3^+PCl_6^-$ and the extended short-chain ionic species $Cl_3PNP(Cl)_2NP(Cl)_2NPCl_3^+PCl_6^-$. These intermediates were identified early in the reaction, but could not be detected after 15 min. Cyclic phosphazenes were detected in low concentrations in the early stages in the reaction, and they increased in concentration to become the major products as the reaction approached completion. No PCl_5 was detected throughout the entire reaction.

These results imply that the mechanism of the reaction can be described as shown in Scheme 2. This mechanism is similar to one first proposed by Becke-Goehring and Fluck for the interaction of PCl_5 with NH_4Cl.[15] In the first step, PCl_5 reacts rapidly with $N(SiMe_3)_3$ to form **2**. The reaction of **2** with PCl_5 to form the short chain $Cl_3PNPCl_3^+PCl_6^-$ salt competes with the first step. This second step occurs at a slightly faster rate than the first. This has been verified by the reaction of an equimolar amount of $N(SiMe_3)_3$ and **2** with PCl_5 monitored by ^1H NMR. After 30 min, integration of the NMR spectrum showed that the **2** was consumed slightly faster than the $N(SiMe_3)_3$.

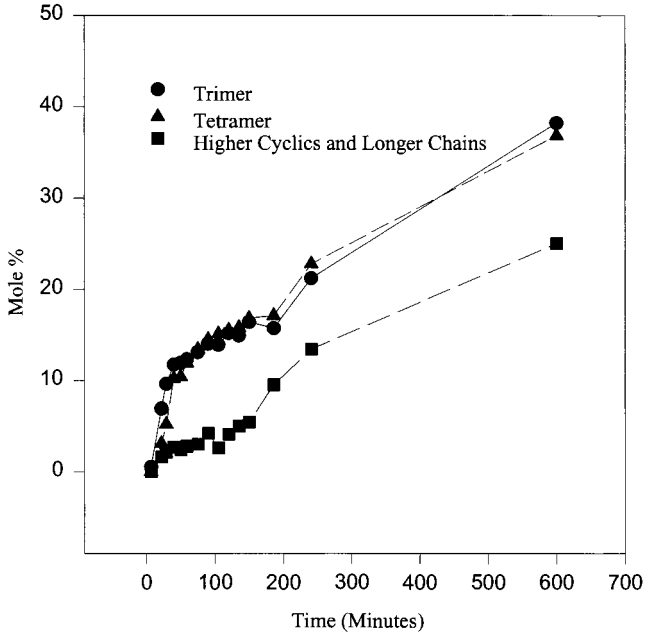

Figure 1. Mol % of cyclic species versus time as monitored by NMR.

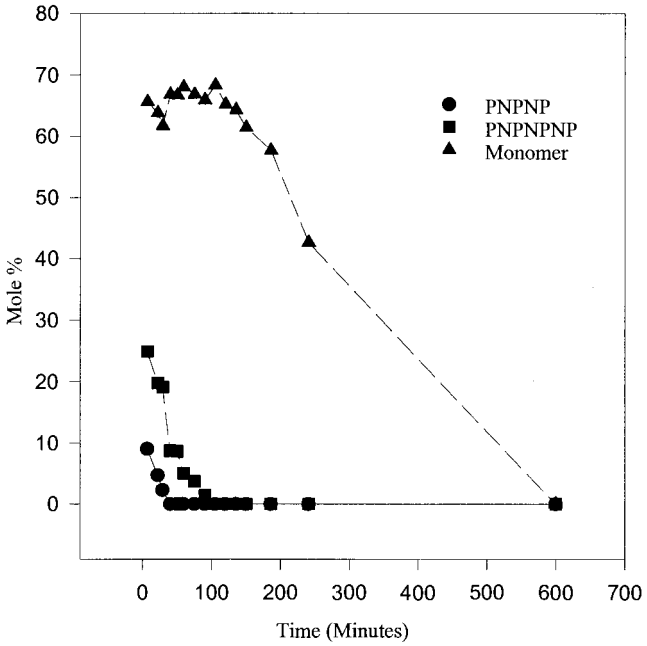

Figure 2. Mol % of linear species versus time as monitored by NMR.

If the reaction is allowed to continue at room temperature, **2** adds to the growing short chain oligomers to increase their length. These short chains can also cyclize in the presence of $N(SiMe_3)_3$. As a cyclic phosphazene is formed, PCl_5 is released. Although no direct evidence exists for the formation of PCl_5, indirect evidence can be found. Because PCl_5 is not detected at any time from the ^{31}P NMR spectra of the reaction mixture, any PCl_5 formed must react rapidly with either

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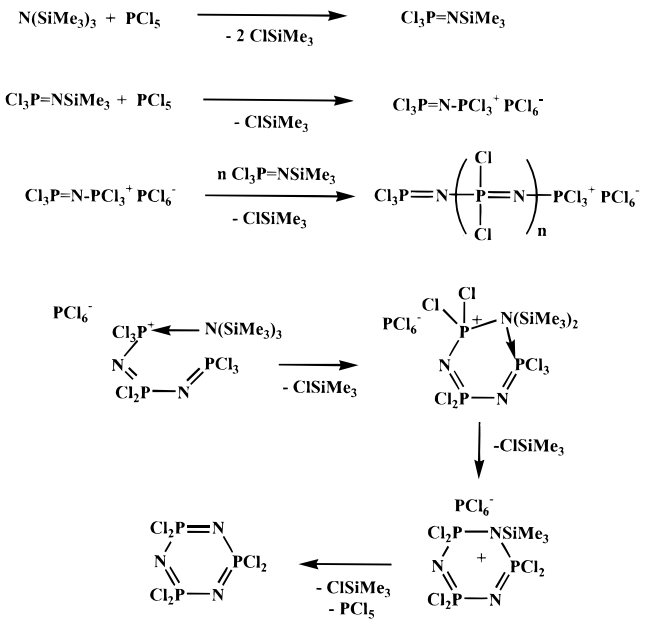
Scheme 2



$N(SiMe_3)_3$ or with **2** and is removed from the reaction mixture. The cyclic trimeric phosphazene is relatively stable under these conditions, and does not react appreciably with any of the other species present in the mixture.

The cyclization step of the reaction mechanism still remained in question. Two different cyclization mechanisms are described in the literature. Emsley suggested an intramolecular cyclization.[16] If this reaction occurred readily at room temperature, the living cationic polymerization to form linear polymer would produce cyclic products. From our experience,[8] cyclic small molecule compounds are seldom detected in this polymerization. Becke-Goehring and Fluck proposed another cyclization mechanism[15] similar to Scheme 2, but with NH_3 as a reactant instead of $N(SiMe_3)_3$. To determine which pathway this reaction follows, two experiments were performed. Species $Cl_3PNP(Cl)_2NPCl_3^+PCl_6^-$ was first synthesized by a previously reported method.[17] Species $N(SiMe_3)_3$ was added to a portion of this material at room temperature in CH_2Cl_2. This reaction yielded primarily the cyclic trimer, together with a small amount of the cyclic tetramer. Unreacted $Cl_3PNP(Cl)_2NPCl_3^+PCl_6^-$ and $Cl_3PNP(Cl)_2NP(Cl)_2NPCl_3^+PCl_6^-$ were also detected. This experiment provided two conclusions: (1) The short chain oligomer reacts with $N(SiMe_3)_3$ to form the stable cyclic trimer. (2) The PCl_5 that is formed as a byproduct of this reaction reacts rapidly with $N(SiMe_3)_3$ to form **2**. Compound **2** then increases the chain length of the oligomer to form $Cl_3PNP(Cl)_2NP(Cl)_2NPCl_3^+PCl_6^-$, which can also cyclize by reaction with $N(SiMe_3)_3$ to form the cyclic tetramer.

The second experiment involved a reaction of $Cl_3PNP(Cl)_2NPCl_3^+PCl_6^-$ with an additional equivalent of **2** in an attempt to form $Cl_3PNP(Cl)_2NP(Cl)_2NPCl_3^+PCl_6^-$. This reaction yielded a mixture of products, $Cl_3P[NP(Cl)_2]_nNPCl_3^+PCl_6^-$, with $n = 0, 1, 2$. The mixture was then heated to reflux in CH_2Cl_2 for 24 h to determine if the linear oligomer undergoes intramolecular cyclization to form the cyclic trimer as suggested by Emsley. No evidence for the cyclic trimer was found in the ^{31}P NMR spectrum after 24 h at reflux in CH_2Cl_2. In fact, no change of any kind occurred in the ^{31}P NMR spectrum. Thus, these two experiments verify the cyclization step of the proposed mechanism.

III. Optimization of the Cyclic Trimer Formation. The complexity of this reaction makes it difficult to favor the formation of either **1** or **2**. An increase in the yield of **1** requires the avoidance of an excess of **2**. If **2** is present in excess, the short chain species $Cl_3PNP(Cl)_2NPCl_3^+PCl_6^-$ will grow through the addition of monomer, rather than undergoing cyclization through reaction with $N(SiMe_3)_3$. However, the formation of cyclic trimer can be favored by the addition of PCl_5 very slowly to $N(SiMe_3)_3$ at reflux temperature in a polar solvent, such as methylene chloride. This allows the linear $Cl_3PNP(Cl)_2NPCl_3^+PCl_6^-$ salt to react with $N(SiMe_3)_3$ and form the cyclic trimer. If PCl_5 is added too quickly, the cyclic tetramer becomes the primary product. This method gives a product mixture that is 76% cyclic trimer, 4% tetramer, 3% pentamer, 5% hexamer, and 12% higher cyclics plus linear oligomers. This reaction has been scaled up to 170 g of PCl_5 and 180 g of $N(SiMe_3)_3$ which provided similar results.

IV. Optimization of the Formation of the Phosphoranimine Monomer. The formation of **2** is favored by the addition of an excess of hexane to the reaction mixture soon after the fast addition of $N(SiMe_3)_3$ to PCl_5 in methylene chloride. An excess of PCl_5 also is favorable, because this ensures that all the $N(SiMe_3)_3$ is consumed. Unreacted $N(SiMe_3)_3$ is difficult to separate from **2** by distillation, but unreacted PCl_5 precipitates from solution when the hexane is added to the reaction mixture. After the hexane addition, the reaction mixture is then distilled to provide **2** in a 40% yield.

Summary

A new method for the synthesis of hexachlorocyclotriphosphazene (**1**) has been found. This approach produces higher yields of **1**, and at lower temperatures than previous methods. Under different reaction conditions, the same reactants form a purer $Cl_3P{=}NSiMe_3$ (**2**) than has been available through other procedures. The major side product of these reactions, Me_3SiCl, can be recycled to form one of the starting materials, $N(SiMe_3)_3$.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide, chlorotrimethylsilane, and phosphorus pentachloride were obtained from Aldrich and were used without further purification. Tetrahydrofuran and hexane (Aldrich) were distilled into the reaction flask from sodium benzophenone ketyl in an atmosphere of dry argon. Dichloromethane and cyclohexane (Aldrich) were dried and distilled from CaH_2 into the reaction flask.

All glassware was dried overnight in an oven- or flame-dried under vacuum before use. The reactions were performed using standard Schlenk techniques or in an inert atmosphere glovebox (Vacuum Atmospheres) under an atmosphere of dry argon or nitrogen.

Equipment. ^{31}P, ^{13}C, and ^1H spectra were recorded with use of a Bruker WM-360 NMR operated at 146, 90.27, and 360 MHz, respectively. ^1H and ^{13}C NMR spectra are referenced to an internal $CDCl_3$. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference.

Preparation of $N(SiMe_3)_3$. Tris(trimethylsilyl)amine was synthesized as reported in the literature, with the exception of an extended reaction time of 72 h.[18]

Reaction of $N(SiMe_3)_3$ with PCl_5. Phosphorus pentachloride in dichloromethane was added to tris(trimethylsilyl) amine in dichloromethane solvent and the mixture was stirred by means of a magnetic stirrer. The addition rates, solvent, and reaction temperatures were varied to favor the formation of either $Cl_3P{=}NSiMe_3$ or $(NPCl_2)_3$.

Optimization of the Formation of Trimer. Tris(trimethylsilyl)-amine (34.00 g, 0.146 mol) was dissolved in methylene chloride (200 mL). The solution was heated to reflux. A solution of phosphorus pentachloride (30.31 g, 0.146 mol) dissolved in methylene chloride (400 mL) was added at a rate of one drop per 2 s over 7 h. The reaction mixture was allowed to reflux for 8 h after the addition and the product was recovered by distillation. ^{31}P NMR: $\delta = +20.7$ (s, $N_3P_3Cl_6$,76%), -6.0 (s, $N_4P_4Cl_8$, 4%), -14.8 (s, $N_6P_6Cl_{12}$, 5%), -16.7 (s, $N_5P_5Cl_{10}$, 3%), -17.5 ppm (mult, higher linears and cyclics, 12%).

Optimization of the Formation of $Cl_3P{=}NSiMe_3$. Phosphorus pentachloride (15.84 g, 0.076 mol) was dissolved in methylene chloride (200 mL), and the solution was stirred and cooled to 0 °C. A solution of tris(trimethylsilyl)amine (8.80 g, 0.038 mol) in methylene chloride (100 mL) was added by addition funnel over a period of 10 min. Freshly distilled hexane (500 mL) was then added to the reaction mixture, and

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this induced the formation of a precipitate. The solution was then filtered with the use of an airless fritted funnel, and the filtrate was distilled at room temperature under vacuum to provide $Cl_3P{=}NSiMe_3$ in 40% yield. ^{1}H NMR ($CDCl_3$): $\delta = 0.18$ ppm (d, $^4J_{PH} = 1$ Hz). ^{31}P NMR ($CDCl_3$): $\delta = -54$ ppm (s). ^{13}C NMR ($CDCl_3$): 1.9 ppm (d, $^4J_{CP} = 7$ Hz, $Si{-}CH_3$).

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