"Living" Cationic Polymerization of Phosphoramidines as an Ambient Temperature Route to Polyphosphazenes with Controlled Molecular Weights


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A new method for the synthesis of poly(dichlorophosphazene) at ambient temperatures is described. The molecular weight of poly(dichlorophosphazene) was controlled by altering the ratio of monomer to initiator. The polymer chains were found to be active after chain propagation since further addition of monomer resulted in the formation of higher molecular weight polymer. Integration of $^1$H and $^{31}$P NMR spectra of these reactions revealed that the polymerization follows first order reaction kinetics with respect to monomer concentration.
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"LIVING" CATIONIC POLYMERIZATION OF PHOSPHORANIMINES AS AN AMBIENT TEMPERATURE ROUTE TO POLYPHOSPHAZENES WITH CONTROLLED WEIGHS

by

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"Living" Cationic Polymerization of Phosphoranimines as an Ambient Temperature Route to Polyphosphazenes with Controlled Molecular Weights.

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Abstract

A new method for the synthesis of poly(dichlorophosphazene) at ambient temperatures is described. It involves the initiation of Cl₃P=NSiMe₃ with trace amounts of PCl₅ in CH₂Cl₂ to yield poly(dichlorophosphazene), [NPCl₂]ₙ, with narrow polydispersities. The molecular weight of poly(dichlorophosphazene) was controlled by altering the ratio of monomer to initiator. The polymer chains were found to be active after chain propagation since further addition of monomer resulted in the formation of higher molecular weight polymer. Integration of ¹H and ³¹P NMR spectra of these reactions revealed that the polymerization follows first order reaction kinetics with respect to monomer concentration. Active polymer chains may be quenched or end-capped by the addition of trace quantities of Me₂(CF₃CH₂O)P=NSiMe₃ or (CF₃CH₂O)₃P=NSiMe₃. Furthermore, PBr₅, SbCl₅ and Ph₃C[PF₆] were also found to be effective initiators in CH₂Cl₂ at room temperature.
Introduction

Polyphosphazenes are inorganic-organic polymers based on the repeating unit \([N=PR_2]_n\), where \(R\) can be halogeno, organic, or organometallic units. Macromolecular substitution reactions carried out on poly(dichlorophosphazene) have been the method of choice for preparing many polymers with side groups such as OR, NHR, or NRR' (Scheme 1). The properties of these polymers vary widely following changes in the side group (R). Properties such as hydrophobicity, hydrophilicity, crystallinity and optical characteristics can be controlled by the nature of the side group.\(^1\)

The most fully developed and commercially feasible route to poly(dichlorophosphazene) makes use of the thermal ring-opening polymerization of hexachlorocyclotriphenphosphazene, \((N=PCl_3)_3\), at 250 °C, which yields poly(dichlorophosphazene) \([N=PCl_2]_n\), but with little or no molecular weight control and with large polydispersities.\(^2\) Some molecular weight control can be achieved by the use of initiators such as OP(OPh)_3/BCl_3 for the ring-opening process.\(^3\) An alternative route to poly(dichlorophosphazene) is through the condensation polymerization of Cl_3P=N-P(O)Cl_2. In this case also some molecular weight control can be achieved, but high temperatures are required and the polydispersities of the resultant polymer are usually higher than 2.\(^4\) The reaction of PCl_5 with ammonium chloride at elevated temperatures has been described as an alternative pathway to low and medium molecular weight \([N=PCl_2]_n\).\(^5,6\) Routes are also available for the direct synthesis of poly(aryl/alkyl)phosphazenes via the condensation polymerization of N-silylphosphoranimines at ca 200 °C, developed by Neilson and Wisian-Neilson,\(^7,8\) which gives polymers with \(M_n\sim10^5\) and with polydispersity indices of 1.5 - 3.0. Matyjaszewski and coworkers\(^9\) have recently reported that phosphoranimine species, such as \((CF_3CH_2O)_3P=NSiMe_3\), undergo cationic polymerizations at 100 °C that produce \([N=P(OCH_2CF_3)_2]_n\) with molecular weights \((M_n)\) that approach 1.0 - 5.0 \(\times\) 10^4 and with polydispersities of 1.2 to 2.5.
Because of the substantial number of polymers accessible through the macromolecular substitution of poly(dichlorophosphazene), improved methods for the synthesis of this polymer would be a significant development from both the scientific and industrial points of view. Moreover, the possibility for control of the molecular weight of poly(dichlorophosphazene) is a key requirement for the further development of this branch of polymer chemistry. An ambient temperature polymerization route may also serve as an efficient method for the large-scale production of a wide variety of polymeric phosphazene systems including block copolymers.

In this paper, as a development of discoveries reported in our initial 1995 communication, we report a new method for the synthesis of poly(dichlorophosphazene). This advanced synthesis takes place at ambient temperatures, allows molecular weight control, and provides polymers with narrow polydispersities. The process can also be used for the direct room-temperature synthesis of organic-substituted polyphosphazenes and for the preparation of block copolymers, as will be reported in another article.

Results and Discussion

The phosphoramidine Cl$_3$P=NSiMe$_3$ (1) is known to react with two equivalents of PCl$_5$ to form [Cl$_3$P=NP-PCl$_3$]+[PCl$_6$]$^-$ with the elimination of Me$_3$SiCl. This ionic species will then interact with an additional equivalent of 1 to eliminate Me$_3$SiCl and form the short chain cationic species [Cl$_3$P=N-PCl$_2$=N-PCl$_3$]$^+$. Oligomeric products can be obtained by the addition of further equivalents of 1 to this species. In view of these results it was postulated that the reaction of 1 with a trace amount of PCl$_5$ should yield high molecular weight polymer.

Synthesis and Polymerization of the Phosphoranimine Cl$_3$P=NSiMe$_3$ (1).

i) Synthesis and Purification. Compound 1 was synthesized initially from Li(N(SiMe)$_3$)$_2$ and PCl$_5$ in hexane at -78 °C. A major challenge was the need to obtain 1 in
high purity. The monomer formed by this route did not polymerize in a reproducible manner when treated with trace amounts of PCl₅ in CH₂Cl₂. ¹H NMR spectra and mass spectrometry (CI-MS) revealed the presence of (Me₃Si)₂NCl as a side product. This species appears to inhibit polymerization. Multiple distillations did not remove (Me₃Si)₂NCl because this compound distills at a similar temperature and pressure to 1. Pure 1 was obtained by treatment of the mixture with PPh₃ (in an excess or stoichiometric amount relative to (Me₃Si)₂NCl) in CH₂Cl₂ to form Ph₃P=NSiMe₃ and Me₃SiCl.¹⁴ The resultant mixture was then distilled at reduced pressure to yield pure 1. Alternatively, to avoid the additional purification step, 1 has also been obtained from the reaction of PCl₅ with N(SiMe₃)₃ in hexane at -78 °C. Although this synthesis generated no (Me₃Si)₂NCl impurity, the yields of 1 produced via this route have not been optimized. Work toward the further development of this synthetic procedure is in progress and will be described in the near future.¹⁵

ii) Bulk Polymerization of Cl₃P=NSiMe₃ (1). The addition of a trace of PCl₅ (ca. 10 mg) to pure 1 (1.0 g) at room temperature led within 24 h to the formation of a two-phase mixture. Both phases were clear and colorless, but the upper, more fluid layer was found by ¹H NMR spectroscopy to consist of Me₃SiCl. A ³¹P NMR spectrum of the entire tube contents comprised a sharp singlet with a chemical shift at -17.4 ppm that was characteristic of poly(dichlorophosphazene). Thus, the conversion of 1 to linear polymer was essentially quantitative. The product was treated with an excess of sodium trifluoroethoxide to replace the chlorine atoms by trifluoroethoxy groups and generate a hydrolytically stable derivative, and the resultant species yielded a ³¹P NMR signal (-6.9 ppm) characteristic of the well-known polymer [N=P(OCH₂CF₃)₂]ₙ (2). Analysis of 2 by gel permeation chromatography (GPC) indicated that it possessed a high molecular weight fraction only, with Mₙ = 1.2 x 10⁵ and a polydispersity index (PDI = Mₘ/Mₙ) of 1.8 versus polystyrene standards. However, in subsequent attempts to obtain lower molecular weight
poly(dichlorophosphazene) by decreases in the ratio of monomer to PCl₅, using the same solvent-free conditions, the initiator and initial cationic products remained primarily immiscible. The molecular weight values of the polymers produced were lower than described above but the GPC chromatogram in this case was multimodal in nature. These results suggested a lack of molecular weight control in the bulk phase due to the heterogeneous nature of the process.

iii) Solution Polymerization Cl₃P=NSiMe₃ (1). In view of the heterogeneous nature of the bulk polymerization, solution reactions appeared to be a possible alternative for controlling the course of the polymerization. Various solvents were investigated for the polymerization of monomer 1 initiated by traces of PCl₅. These included methylene chloride, cyclohexane, tetrahydrofuran, acetonitrile, and nitromethane to examine the effect of solvent polarity and dielectric strength on the rate of the polymerization. Reactions conducted with a 50:1 molar ratio of 1 to PCl₅ were monitored by ³¹P NMR spectroscopy. Only in CH₂Cl₂ or cyclohexane did the polymerizations proceed quantitatively without side reactions. The polymerization in CH₂Cl₂ was complete within 4 h at 25 °C, while in cyclohexane the polymerization reached completion in about 24 h. The reaction rate is thought to be faster in CH₂Cl₂ than in cyclohexane because of the higher polarity, dielectric strength, and solvating ability of CH₂Cl₂. In the other media it appeared that the solvent itself reacted with either the monomer, the initiator, and/or the growing polymer chain (See Table I). Also, in the solution polymerization of 1 in CH₃CN or CH₃NO₂, the poly(dichlorophosphazene) was not completely soluble. The presence of suitable donor solvents may accelerate the reaction by causing greater ion pair separation.

Structures 1 and 2 near here.

Table I near here.
However, the reaction of 1 with traces of PCl₅ in CH₂Cl₂ resulted in a quantitative conversion to poly(dichlorophosphazene) as estimated by ¹H and ³¹P NMR spectroscopy and by GPC analysis of the trifluoroethoxy derivative 2. Very narrow polydispersities (PDI < 1.32) were obtained. An increase in the ratio of phosphoranimine to PCl₅ in solution brought about an increase in the molecular weight, while still retaining narrow PDI values (see Table II).

The calculated molecular weights shown in Table I were predicted on the basis of monomer to initiator ratios, and these differed from the values determined by gel permeation chromatography (GPC). The molecular weight values obtained by GPC were estimated versus polystyrene standards and this could account for the difference between the calculated and the found values.¹⁶,¹⁷ Molecular weights of short chain polymers and oligomers obtained by ³¹P NMR spectroscopy based on the end group to middle unit ratios correspond more closely to the expected values. For example, a ³¹P NMR spectrum of a 20:1 1:PCl₅ ratio sample contained small peaks at +9 ppm (d, -PCl₃ terminal), -14 ppm (t, -PCl₂·PCl₃), and -15 ppm (t, PCl₂·PCl₂·PCl₃), along with an intense peak at -17 ppm (br, s, -(PCl₂)ₙ⁻), characteristic of the known resonance for the middle units of the polymer chain [N=PCl₂]ₙ. The peak ratios determined by integration is 1:1:1:17, which corresponds well to the theoretical structure for a 40 repeat unit macromolecule.

Table II near here.

iv) Effect of the Type of Initiator on the Solution Polymerization of 1.

A number of initiators have been examined for the ambient temperature polymerization of 1 including Lewis acidic main group and transition metal chlorides, as well as a number of trityl cations (see Table III). Phosphorane species such as PX₅ (X = Cl, Br) rapidly initiate the polymerization of 1. Previous work has shown that the reaction
of the phosphoranimine 1 with two equivalents of PCl₅ results in the formation of [Cl₃P=N-PCl₃]⁺ [PCl₆]⁻.¹¹,¹³ Successive additions of 1 and 2 equivalents of 1 yield the oligomeric species [Cl₃P(NPCl₂)ₓ-NPCl₃]⁺[PCl₆]⁻, with x = 2 and 3, respectively.¹¹ A reaction of 1 with PhPCl₄ in a 10:1 molar ratio produced poly(dichlorophosphazene) which, after treatment with NaOCH₂CF₃ was found to possess a Mₙ = 1.2 x 10³ and PDI = 1.03. This suggests that the cationic initiation method is relatively insensitive to the nature of the phosphorane employed. Other Group V chlorides such as SbCl₅ were also found to be efficient initiators for the polymerization of 1. For example, in an attempt to compare the reactivity of PCl₅ and SbCl₅ toward 1, two separate samples of 1 were treated with 5 % molar equivalents of PCl₅ and SbCl₅ in CH₂Cl₂. Both reactions proceeded at similar rates and were complete within 1.5 h, as indicated by the disappearance of the ⁳¹P NMR resonance for 1 at -54 ppm. After treatment of the resultant [N=PCl₂]ₙ with sodium trifluoroethoxide, the GPC molecular weights and polydispersities for the PCl₅- and SbCl₅-induced polymerizations were found to be very similar. The PCl₅-induced polymerization produced [N=P(OCH₂CF₃)₂]ₙ (2) with an Mₙ of 2.3 x 10⁴ (PDI = 1.03) within 1.5 h and the SbCl₅-initiated polymerization produced a counterpart with a Mₙ of 1.8 x 10⁴ but with a slightly higher PDI value (PDI = 1.11) within the same 1.5 h. Interestingly, high oxidation state transition metal halides such as TiCl₄, Cp₂TiCl₂, TaCl₅, WCl₆, VCl₄ and main group Lewis acids, such as dibutylboron triflate (Bu₂BOSO₂CF₃), POCl₃, AlCl₃, Et₂AlCl, SnCl₄ and SnCl₂, did not initiate the polymerization of 1 at room temperature but instead reacted with Cl₃P=NSiMe₃ in refluxing CH₂Cl₂ to produce macromolecules with lower molecular weights and broader polydispersities than those obtained by the ambient temperature route. For example, a 20:1 ratio of 1:VCl₄ at 60 °C yielded poly(dichlorophosphazene) which, after treatment with NaOCH₂CF₃, had an Mₙ of 6.0 x 10³ (PDI = 1.23). These differences in initiation behavior suggest that a key requirement for polymerization initiation is the ability of the initiator to form multiple bonds with nitrogen in a similar fashion to the formation of the cationic species [Cl₃P=N-PCl₃]⁺ [PCl₆]⁻.¹¹ Previous phosphoranimine reactivity studies
have shown that the phosphoranimine 1 reacts with BX₃, WCl₆, or TaCl₅ to form stable neutral adducts Cl₃P=N-MXₙ (M = B, Xₙ = X₂; M = W, Xₙ = Cl₅; M = Ta, Xₙ = Cl₄).

Several trityl salts were also found to react with 1 at 25 °C. Reaction of Ph₃C[PF₆] (5 mol %) with 1, followed by polymerization for 4 h and halogen replacement, yielded 2 in ca. 80 % yield (Mₙ = 1.6 x 10⁴; PDI = 1.08), with the remaining 20 % consisting of the cyclic species (N=PCl₂)ₓ identified by their ³¹P NMR resonances (x = 3, 20.8 ppm and x = 4, - 7.1 ppm respectively). In a similar experiment 1 was treated with Ph₃C[SbCl₆] (20 mol %) in CH₂Cl₂ and the reaction was monitored by ³¹P NMR spectroscopy over a 24 h period. The hexachloroantimonate trityl salt produced mainly cyclic species (N=PCl₂)₃,₄ and linear oligomers as determined by GPC and ³¹P NMR experiments. The fact that the trityl-based cations produce cyclic phosphazenes may provide evidence for an alternative mechanism when these carbocations are present. The carbocations may simply react with 1 via attack at nitrogen to produce a reactive intermediate such as (Cl₃P=N⁺), as reported for the high temperature cationic polymerization of tris(organo)phosphoranimines by Matyjaszewski and coworkers. Such an intermediate in our polymerizations would then interact with further equivalents of 1 via reaction at phosphorus to produce Me₃SiCl and a growing, even-numbered oligomer [N=PCl₂]ₙ. This proposed mechanism contrasts with the PCl₅-induced polymerizations in the sense that, with phosphorane catalysts, odd numbered chains are produced, such as [(Cl₂P=N)ₓ-PCl₃]⁺[PCl₆]⁻ (x = 1, 2, etc.), thus limiting the opportunity for even-numbered oligomeric species to be formed, and this could favor the formation of cyclic species via back-biting or other cyclization reactions (see Scheme 2). Also, in the high temperature cationic polymerizations that employ Ph₃C[SbCl₆] as an initiator, the trityl salt was reported not to be the active initiator, but rather SbCl₅ formed through an equilibrium with the hexachloroantimonate salt. Clearly no such equilibrium exists in our ambient temperature polymerizations based on the efficiency of SbCl₅ -induced polymerizations of 1 mentioned earlier (see Table III).
v) Effect of Temperature on the Solution Polymerization of 1. The influence of temperature changes on the solution polymerization of 1 were examined with a 20:1 ratio of monomer 1 to PCl₅ in CH₂Cl₂. The polymerizations were monitored by ¹H and ³¹P NMR spectroscopy from 15 to 35 °C over the course of the polymerization (See Table IV). Lowering of the temperature increased the times needed for completion of the polymerization, while temperature increases decreased the polymerization times. The PCl₅-induced polymerization of 1 proceeded to completion within 2 h at 15 °C, 1 h at 25 °C, 40 min at 30 °C, and 35 min. at 35 °C. Thus, below room temperature, the polymerization is slow and at even lower temperatures it may be brought to a halt. The measured molecular weight of the polymer increased slightly as the temperature was lowered, but these results are within experimental error.

The effect of temperature decreases on the inhibition of polymerization for a 100:1 1 to PCl₅ ratio reaction was examined at -50 °C and at 25 °C, and was monitored by ¹H and ³¹P NMR spectroscopy. The polymerization at 25 °C was complete in less than 9 h but after the same time at -50 °C only monomer was detected. However, on warming this mixture to 25 °C the monomer was converted to polymer in less than 9 h. Similarly, a 10:1 ratio of 1 to PCl₅ was monitored at low temperatures. The polymerization was initiated at 25 °C and then cooled to -10 °C. After 2 days at -10 °C the polymerization was about 75% complete as determined by ³¹P NMR spectroscopy. At -10 °C the polymerization had slowed dramatically, but was not completely inhibited. The mixture was then cooled to -52 °C and the propagation reaction ceased. The reaction mixture was maintained at -52 °C for one week while the ratio of 1 to poly(dichlorophosphazene) was monitored by ³¹P NMR spectroscopy. The polymerization was inhibited completely at -52 °C. However, again on warming to 25 °C, the propagation resumed and was complete in less than one hour. Thus,
at low temperatures, the chain ends appear to be still active after propagation has ceased. This is strong evidence for a living polymerization.

Table IV near here.

vi) Activity of the Chains. A solution of poly(dichlorophosphazene) in CH₂Cl₂ was prepared via the reaction of 1 with PCl₅ in a 9.3:1 ratio in which all the phosphoranimine had been converted to polymer, as determined by ¹H and ³¹P NMR spectroscopy. A portion of this sample was subjected to halogen replacement replacement as described above to yield a trifluoroethoxy-substituted polymer 2 with Mₙ = 1.1 x 10⁴ and PDI = 1.09. Further addition of phosphoranimine to the remaining polymerization mixture to generate a molar ratio of 1:[NPCl₂]ₙ of 5:1, resulted in the continued conversion of 1 to polymer over 24 h. The GPC analysis of the trifluoroethoxy-derivatized polymer 2 formed from this solution showed the presence of polymer with Mₙ = 4.4 x 10⁴ and PDI = 1.17 with no evidence for the presence of the lower molecular weight polymer. Thus, it appears that the active chain ends can resume chain growth following the addition of more monomer. This opens up many possibilities for control of the chain length and for coupling of the chain ends to other monomers or polymers. In addition, the active chains may be quenched or end-capped with suitable reagents, allowing further molecular weight control and the possibility of further functionalization of the macromolecules.

One possible end-capping species is a tris(organo)phosphoranimine such as (CF₃CH₂O)₃P=NSiMe₃, where the presence of the SiMe₃ group permits reaction with the polymeric cation, while the absence of a chlorine unit at phosphorus should result in termination. Indeed, when a polymerized solution of 1, initiated with a 2 % molar equivalent of PCl₅ in CH₂Cl₂, was treated with trace quantities of (CF₃CH₂O)₃P=NSiMe₃ at regular intervals during the polymerization, the growth of the polymeric cation was quenched as monitored by ³¹P NMR spectroscopy. GPC examination of the resultant
polymers after chlorine replacement with NaOCH₂CF₃ showed a consistent range of molecular weights for the endcapped polymerization (see Table V, Figure 1). Unfortunately, the presence of the terminal \(-N=P(OCH₂CF₃)₃\) group in the end-capped polymer could not be confirmed from the \(^{31}\text{P} \) NMR spectrum of an oligomeric sample of poly(dichlorophosphazene) synthesized from treatment of 1 with a 20\% molar equivalent of PCl₅. The resonance for the terminal \(-N=P(OCH₂CF₃)₃\) species was perhaps concealed by resonances for the oligo(dichlorophosphazene) species. In a further effort to confirm the presence of such endcapping groups, an oligomeric sample of [\(N=\text{PCl}_2\)]ₙ, synthesized by treatment of 1 with a 10\% molar equivalent of PCl₅, was treated with Me₂(CF₃CH₂O)P=NSiMe₃.\(^{21}\) Examination of this endcapped species by \(^{31}\text{P} \) NMR spectroscopy revealed the terminal \(-N=P\text{Me}_2(OCH₂CF₃)\) species from a doublet resonance at 9.4 ppm (Figure 2). The \(M_n\) of this endcapped oligomer was found to be \(5.9 \times 10^3 \) (PDI = 1.05, by GPC) after macromolecular substitution with NaOCH₂CF₃.

Table V near here.

vii) Molecular Weight Changes as a Function of Polymerization Time.
The solution polymerization of 1 with a 46:1 monomer to PCl₅ initiator ratio in CH₂Cl₂ was monitored as a function of time. Aliquots were removed at regular intervals and the chlorine atoms were replaced by treatment with NaOCH₂CF₃. The molecular weights of the resultant polymers were then estimated by GPC. One of the characteristics of a living polymerization is a linear increase in molecular weight with respect to time. This is the situation with this system, as illustrated in Figure 3.

eviii) Percent Monomer Conversion Versus Time. Another characteristic of a living polymerization is that the reaction should follow first order kinetics with respect to monomer concentration. The polymerization of a 100:1 1:PCl₅ sample was
monitored with $^1$H and $^{31}$P NMR spectroscopy. A plot of ln[monomer] versus time
(Figures 4 and 5) showed a linear relationship and this suggests first-order kinetics. The
first order rate constant for this polymerization was found to be $k_{297} = 3.0 \times 10^{-3} \text{s}^{-1}$.

ix) Evidence for Macrocondensation. Samples of poly-
(dicholorophosphazene) that were not subjected to halogen replacement immediately
following complete conversion of monomer, but instead were maintained for several days at
25 °C before being substituted, showed a change in molecular weight distribution. GPC
chromatograms consisted not of a single sharp peak as expected, but a peak with a higher
molecular weight shoulder. The shoulder corresponded to approximately twice the
molecular weight of the original peak. This occurred for several monomer to initiator ratios,
and suggested a macrocondensation reaction in which two polymer chains join together to
form a single polymer of twice the molecular weight. In order to study this phenomenon, a
polymerization experiment was conducted with a 23:1 1:PCl$_5$ ratio sample. The
polymerization solution was divided into two equal parts. The first sample was treated with
NaOCH$_2$CF$_3$ in dioxane immediately after conversion of the monomer to polymer. The
GPC chromatogram of this substituted polymer 2 contained one sharp peak that
corresponded to values of $M_n = 2.0 \times 10^4$ and PDI = 1.09, as seen in Figure 6. The second
sample was not substituted, but was stirred at 25 °C for 20 days in the $[\text{N}=\text{PCl}_2]_n$ form. It
was then treated with NaOCH$_2$CF$_3$ in dioxane to produce polymer with $M_n = 2.2 \times 10^4$ and
PDI = 1.17. However, the GPC chromatogram of this polymer had an additional high
molecular weight shoulder at approximately twice the molecular weight of the first polymer.
This suggests that $[\text{N}=\text{PCl}_2]_n$ macrocondensation can occur over time. A possible
mechanism for this process is hydrolytic coupling of two polymer chains to give a
macromolecule with a molecular weight twice that of the original. Another possibility is the
coupling of two neutral chain ends (Cl$_3$P=N-) to form a dimeric species. This dimerization
is illustrated in Scheme 3. Thus, in order to obtain controlled molecular weight polymers, it
is essential to substitute the polymer immediately after complete conversion of monomer or to store the material at temperatures below 0 °C.

x) **High Molecular Weight Polymers.** Polymerizations at higher ratios of 1 to PCl₅ than 150:1 in CH₂Cl₂ were attempted in order to obtain very high molecular weight polymers. The molecular weights obtained at these higher monomer ratios were not reproducible. However, an alternative method of synthesis provided high molecular weight products, but with a multimodal molecular weight distribution. A 25:1 monomer to initiator sample was allowed to react until complete conversion to polymer had occurred at 25 °C. A fraction of the mixture was then removed for NMR analysis. More monomer 1 was then introduced to the system. ¹H and ³¹P NMR analysis showed that this monomer was also quantitatively converted to polymer. Four additional charges of 1 were added in this fashion over the course of one week (each ca. 25:1 1: [PCl₅]initial). The resultant polymer was then treated with NaOCH₂CF₃ to provide high molecular weight polymer 2 (multimodal GPC trace with peaks at Mₙ = 1.2 x 10⁶, PDI = 1.18; Mₙ = 3.7 x 10⁴, PDI = 1.47; Mₙ = 8.8 x 10³, PDI = 1.01). The highest molecular weight fraction has a molecular weight comparable to that of poly(dichlorophosphazene) formed by the classical ring-opening polymerization method.

xi) **Room Temperature Polymerization of Organic-Substituted Phosphoranimines.** The procedures discussed above also allow organic-substituted monomers such as PhCl₂P=NSiMe₃, Ph₂CIP=NSiMe₃, Me(Et)CIP=NSiMe₃, and (CF₃CH₂O)₂BrP=NSiMe₃ to be polymerized in the same way to give polymers [N=P(Ph)(OCH₂CF₃)]ₙ, [N=P(Ph)₂]ₙ, [N=PMe(Et)]ₙ, and [N=P(OCH₂CF₃)₂]ₙ. This aspect has also been developed in detail, and will reported in a forthcoming publication.¹²
Summary

The cationic polymerization of $\text{Cl}_3\text{P}=\text{NSiMe}_3$ (1), initiated by phosphoranes such as $\text{PCl}_5$, provides access to poly(dichlorophosphazene) with controllable molecular weights and narrow polydispersities. The $\text{PCl}_5$-induced polymerization of 1 has also been shown to display living characteristics. This new synthetic route for the production of well-defined poly(dichlorophosphazene), a key intermediate for the synthesis of hundreds of different macromolecules, has widespread implications for the industrial and academic development of polyphosphazenes. In addition, the ambient temperature method provides an effective direct route to poly(organophosphazenes), via the $\text{PCl}_5$-induced polymerizations of mono- and diorganosubstituted phosphoranimines, an approach that will be discussed in a forthcoming publication. Current work is also focused on the synthesis of phosphazene-based copolymers, including the development of phosphazene-phosphazene and phosphazene-organic block copolymers via this polymerization method.

Experimental Section

Materials

Lithium bis(trimethylsilyl)amide, $\text{TiCl}_4$, $\text{Cp}_2\text{TiCl}_2$, $\text{TaCl}_5$, $\text{WCl}_6$, $\text{VCl}_4$, $\text{SbCl}_5$, dibutylboron triflate (1M solution in dichloromethane), $\text{POCl}_3$, $\text{AlCl}_3$, $\text{Et}_2\text{AlCl}$ (1.8M solution in toluene), $\text{SnCl}_4$, $\text{SnCl}_2$, 2,2,2-trifluoroethanol, sodium metal, and chlorine gas were obtained from Aldrich and were used without further purification. Phosphorus pentachloride (Aldrich) was sublimed under vacuum. $\text{PhPCl}_4$, sodium trifluoroethoxide, $\text{Me}_2(\text{CF}_3\text{CH}_2\text{O})\text{P}=\text{NSiMe}_3$, and $(\text{CF}_3\text{CH}_2\text{O})_3\text{PNSiMe}_3$ were synthesized and purified by literature procedures. 1,4-Dioxane, tetrahydrofuran, and hexane (Aldrich) were distilled into the reaction flask from sodium-benzophenone ketyl in an atmosphere of dry argon. Dichloromethane (Aldrich) was dried and distilled from $\text{CaH}_2$ and then from $\text{P}_2\text{O}_5$ into the reaction flask. Acetonitrile, nitromethane, and cyclohexane (Aldrich) were distilled from $\text{P}_2\text{O}_5$ 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 glove box (Vacuum Atmospheres) under an atmosphere of dry argon or nitrogen.

**Equipment**  
$^{31}$P, $^{13}$C, and $^1$H spectra were recorded with use of a Bruker WM-360 NMR operated at 146, 90.27, and 360 MHz respectively. $^{29}$Si NMR spectra were recorded with use of a Bruker AM-300 NMR operated at 59.6 MHz and were referenced externally to SiMe$_4$. $^1$H 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. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, American Polymer Standards AM gel 10 µm and AM gel 10 µm $10^4$ Å column, and calibrated versus polystyrene standards (Polysciences). The samples were eluted with a 0.1% by weight solution of tetra-n-butylammonium nitrate (Aldrich) in THF (OmniSolv).

**Preparation of Cl$_3$P=NSiMe$_3$ (1).** Compound 1 was synthesized as reported previously, with the modification that the distilled mixture of 1 and (Me$_3$Si)$_2$NCl was treated with PPh$_3$ (amount as determined by $^1$H NMR integration) and the resultant mixture was redistilled at reduced pressure.

For 1; Yield 43%. $^1$H-NMR (CDCl$_3$): $\delta$ = 0.18 ppm (d, $^4$J$_{PH}$ = 1 Hz); $^{31}$P-NMR (CDCl$_3$): $\delta$ = -54 ppm. $^{13}$C-NMR (CDCl$_3$): 1.9 ppm (d, $^4$J$_{CP}$ 7 Hz, Si-CH$_3$); $^{29}$Si (CDCl$_3$): $\delta$ = 0.27 (d, $^2$J$_{PSi}$ = 11 Hz). MS. (Cl, Isobutane): m/z = 224 (MH$^+$, 98 %), 208 (M$^+$ - Me, 82 %), in good agreement with isotopic abundance calculations.

**Polymerization of 1 in Solution and in the Bulk Phase.** a) A solution of 10 mg (0.048 mmol) of PCl$_5$ in 3 mL of CH$_2$Cl$_2$ was placed in a Schlenk flask in a glove
box and was stirred with use of a magnetic stirrer. A solution of 0.2 g (0.89 mmol) of I in 2 mL of CH₂Cl₂ was then added to the flask. The reaction mixture was monitored by ¹H and ³¹P NMR spectroscopy. After complete conversion of I to polymer, all volatiles were removed at reduced pressure. The polymer was then dissolved in 10 ml of dioxane and treated with 2.5 M sodium trifluoroethoxide (10 mmols) in dioxane (4 mL). The mixture was then refluxed for 1 hour, and stirred at 25 °C for 24 hours. The polymer was then precipitated into deionized water (3x) and hexane (2x): Yield 72%. In order to control the molecular weight, the ratio of monomer to initiator was varied by changing the amount of monomer while keeping all other amounts constant.

b) For the polymerization study in a variety of solvents, the above procedure was followed. However, 0.21 g I (0.94 mmol) was dissolved in 2.0 mL of solvent followed by the addition of 1.0 mL of 19 mM PCl₅ (0.0192 mmol) in each respective solvent of i) CH₂Cl₂, ii) cyclohexane, iii) THF, iv) CH₃CN, and v) CH₃NO₂. In all the polymerizations, the resulting [N=PCl₂]ₙ was treated with NaOCH₂CF₃ and was examined by GPC: i) Mₙ = 4.2 x 10⁴ and PDI = 1.18, ii) Mₙ = 3.3 x 10⁴ and PDI = 1.06, iii) Mₙ = 4.4 x 10⁴ and PDI = 1.15, iv) Mₙ = 5.3 x 10⁴ and PDI = 1.02 and v) Mₙ = 2.0 x 10⁴ and PDI = 1.03.

c) The variable temperature experiments were conducted in a 5 mm NMR tube with D₂O in a sealed glass capillary tube as an internal reference at i) 15 ii) 25, iii) 30, and iv) 35 °C. 1 (0.05 g, 0.22 mmol) was dissolved in CH₂Cl₂ (0.5 mL) and placed in a closed tube with a rubber septum followed by the addition via syringe of 0.5 mL of 24 mM PCl₅ in CH₂Cl₂ at -78 °C. The mixture was immediately warmed to the appropriate temperature in the NMR spectrometer and the reactions were monitored by ³¹P and ¹H NMR spectroscopy. The polymerizations were rapid and complete in i) 120, ii) 60, iii) 40, and iv) 35 min. Treatment with NaOCH₂CF₃ of the resulting poly(dichlorophosphazene) was then followed by characterization by GPC: i) Mₙ = 2.5 x 10⁴ and PDI = 1.06, ii) Mₙ = 2.4 x 10⁴ and PDI = 1.05, iii) Mₙ = 2.3 x 10⁴ and PDI = 1.01, and iv) Mₙ = 2.2 x 10⁴ and PDI = 1.01.
Similar procedures were followed for the 100:1 and 10:1 inhibition experiments with 1 (0.05 g, 0.22 mmol) where PCl₅ (0.1 mL 24 mM) in CH₂Cl₂ followed by the addition of CH₂Cl₂ (0.9 mL) and PCl₅ (1.0 mL 24 mM) in CH₂Cl₂ respectively.

d) To a stirred solution of 1 (0.4 g, 1.8 mmol) in CH₂Cl₂ (2 ml) was added a 5% molar equivalent of i) PBr₅ (0.01 g, 0.04 mmol), ii) SbCl₅ (0.01 g, 0.04 mmol), iii) Ph₃CPF₆ (0.02 g, 0.04 mmol), iv) Ph₃CSbCl₆ (0.03 g, 0.04 mmol), v) POCl₃ (ca. 0.007 g, 0.04 mmol), vi) AlCl₃ (ca. 0.005 g, 0.04 mmol), vii) SnCl₄ (0.01 g, 0.04 mmol), viii) SnCl₂ (0.007 g, 0.04 mmol), ix) TaCl₅ (0.02 g, 0.04 mmol), x) VCl₄ (0.008 g, 0.04 mmol), xi) WCl₆ (0.02 g, 0.04 mmol), xii) TiCl₄ (0.009 g, 0.04 mmol), xiii) Cp₂TiCl₂ (0.01 g, 0.04 mmol), and xiv) Bu₂BOSO₂CF₃ (40 µL of 1.0 M solution in CH₂Cl₂, 0.04 mmol). In the case of i) - iii) the polymerizations proceeded rapidly to completion (for i) - ii) within 1.5 h; 3.5 h for iii)) and treatment of the resultant [N=PCl₂]ₙ with NaOCH₂CF₃ produced 2 thus permitting molecular weight determination by GPC.

GPC for 2: i) Mₙ = 1.8 x 10⁴ and PDI = 1.13, ii) Mₙ = 1.8 x 10⁴ and PDI = 1.11, iii) Mₙ = 1.6 x 10⁴ and PDI = 1.06. In the case of iv) only oligomeric species and cyclic species, (N=PCl₂)₃,₄, were produced based on the solubility of the resultant products in hexanes and upon confirmation by ³¹P NMR and GPC. In the case of v) - xiv) no polymerization behavior was detected over 48 h when monitored periodically by ³¹P NMR. In addition, polymerization of 1 was attempted with a 15% molar amount of VCl₄ in refluxing CH₂Cl₂ over the span of 4 hrs produced [N=PCl₂]ₙ which was substituted with NaOCH₂CF₃ and was found to possess Mₙ = 6.0 x 10³ (PDI = 1.23).

Attempted Endcapping of the PCl₅-induced Polymerization of 1 with the Phosphoranimine Species (CF₃CH₂O)₃P = NSiMe₃ and Me₂(CF₃CH₂O)P = NSiMe₃.

a) To a stirred solution of 1 (1.1 g, 4.9 mmol) in 1 ml CH₂Cl₂ was added a 2% molar equivalent of PCl₅ (ca. 0.02 g, 0.1 mmol) at room temperature. At various time intervals, an aliquot of the reaction mixture was treated with
(CF<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>P=NSiMe<sub>3</sub> (ca. 0.02 g) and was examined by $^{31}$P NMR spectroscopy immediately and again 24 h later to ensure termination. The reaction mixture was found to contain: i) at 1.25 h [N=PCl<sub>2</sub>]<sub>n</sub> (30 %) and 1 (70 %); GPC: $M_n = 2.6 \times 10^4$ and PDI = 1.06. ii) at 2.5 h [N=PCl<sub>2</sub>]<sub>n</sub> (36 %) and 1 (64 %); GPC: $M_n = 3.2 \times 10^4$ and PDI = 1.05. iii) at 3.75 h [N=PCl<sub>2</sub>]<sub>n</sub> (95 %) and 1 (5 %); GPC: $M_n = 3.8 \times 10^4$ and PDI = 1.03.; and iv) at 24 h [N=PCl<sub>2</sub>]<sub>n</sub> (100 %); GPC: $M_n = 4.0 \times 10^4$ and PDI = 1.02. The relative quantities of [N=PCl<sub>2</sub>]<sub>n</sub>:1 remained consistent over a 24 h period as monitored by $^{31}$P NMR spectroscopy. The presence of the terminal -N=P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> in these experiments could not be confirmed by $^{31}$P NMR.

b) To a stirred solution of 1 (0.2 g, 0.9 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (1 ml) was added a 10 % molar equivalent of PCl<sub>5</sub> (ca. 0.02, 0.1 mmol) at room temperature. After 30 min. an aliquot of the reaction mixture was quenched with Me<sub>2</sub>(CF<sub>3</sub>CH<sub>2</sub>O)P=NSiMe<sub>3</sub> (ca. 0.02 g) and was examined immediately by $^{31}$P NMR spectroscopy. $^{31}$P-NMR (CH<sub>2</sub>Cl<sub>2</sub>): $\delta = 9.4$ (d, $^2J_{PP} = 40$ Hz, -N=PMe<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)), -14.2 (t, $^2J_{PP} = 43$ Hz, -N=PCl<sub>2</sub>-N=PMe<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)), -15.2 (d, $^2J_{PP} = 40$ Hz, [-N=PCl<sub>2</sub>-N=PCl<sub>2</sub>-N=PMe<sub>2</sub>(OCH<sub>2</sub>CF<sub>3</sub>)]) and -16.6 - -17.3 (br s, [N=PCl<sub>2</sub>]<sub>n</sub>). Subsequent substitution with NaOCH<sub>2</sub>CF<sub>3</sub> resulted in the formation of 2. GPC: $M_n = 5.9 \times 10^3$ and PDI = 1.05.

References


(16) The discrepancy between theoretical and experimentally obtained molecular weights (GPC) is thought to be due to an overestimation by gel permeation chromatography versus polystyrene standards. Previous examinations of [N=P(OCH₂CF₃)₂]ₙ by light scattering techniques provided absolute molecular weight measurements which were also higher than the molecular weights obtained by GPC (vs. polystyrene, see Ref. 17).


Cl\quad P=N\text{SiMe}_3 \quad \xrightarrow{i)} \text{Trace PCl}_3/\text{CH}_2\text{Cl}_2 \quad \xrightarrow{\text{ii)}} \text{NaOCH}_2\text{CF}_3/\text{dioxane} \quad \begin{array}{c}
\text{OCH}_2\text{CF}_3 \\
\text{OCH}_2\text{CF}_3 \quad \text{n}
\end{array}
Table I. Solvent Effects on the Ambient Temperature Solution Polymerization of $\text{Cl}_3\text{P}=$NSiMe$_3$ (1).

<table>
<thead>
<tr>
<th>M:I</th>
<th>Solvent</th>
<th>% Yield Polymer$^a$</th>
<th>$M_n \times 10^{-4}$ Found</th>
<th>$M_n \times 10^{-4}$ Calculated$^b$</th>
<th>Reaction Time h</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>50:1</td>
<td>CH$_2$Cl$_2$</td>
<td>ca. 100</td>
<td>4.2</td>
<td>2.4</td>
<td>4</td>
<td>1.18</td>
</tr>
<tr>
<td>50:1</td>
<td>Cyclohexane</td>
<td>ca. 100</td>
<td>3.3</td>
<td>2.4</td>
<td>24</td>
<td>1.06</td>
</tr>
<tr>
<td>50:1</td>
<td>THF</td>
<td>72</td>
<td>4.4</td>
<td>2.4</td>
<td>48</td>
<td>1.15</td>
</tr>
<tr>
<td>50:1</td>
<td>CH$_3$CN</td>
<td>50</td>
<td>5.3</td>
<td>2.4</td>
<td>48</td>
<td>1.02</td>
</tr>
<tr>
<td>50:1</td>
<td>CH$_3$NO$_2$</td>
<td>50</td>
<td>2.0</td>
<td>2.4</td>
<td>48</td>
<td>1.03</td>
</tr>
</tbody>
</table>

$^a$Yields determined by $^{31}$P NMR integration.

$^b$Calculated from the initial ratio of monomer to PCl$_5$ initiator.
Table II. Effect of Monomer to Initiator Ratio on the Molecular Weight Polymerization of Cl$_3$P=NSiMe$_3$ (1).$^a$

<table>
<thead>
<tr>
<th>M:I</th>
<th>$M_n \times 10^{-3}$ Found$^b$</th>
<th>$M_n \times 10^{-3}$ Calculated$^c$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>4.6:1</td>
<td>5.8</td>
<td>2.5</td>
<td>1.20</td>
</tr>
<tr>
<td>9.3:1</td>
<td>10.6</td>
<td>5.0</td>
<td>1.04</td>
</tr>
<tr>
<td>23:1</td>
<td>20.2</td>
<td>12</td>
<td>1.09</td>
</tr>
<tr>
<td>46:1</td>
<td>53.0</td>
<td>24</td>
<td>1.32</td>
</tr>
<tr>
<td>70:1</td>
<td>66.4</td>
<td>36</td>
<td>1.25</td>
</tr>
</tbody>
</table>

$^a$See Experimental Section for details.

$^b$Obtained by GPC vs polystyrene standards.

$^c$Calculated from the initial ratio of monomer to PCl$_5$ initiator.
Table III  Effect of Initiator on the Ambient Temperature Solution Polymerization of Cl₃P=NSiMe₃ (1).

<table>
<thead>
<tr>
<th>M:I</th>
<th>Initiator</th>
<th>% Yield 2ᵃ</th>
<th>$M_n \times 10^{-4}$ Found</th>
<th>$M_n \times 10^{-3}$ Calculatedᶜ</th>
<th>PDI</th>
<th>Reaction Time (h)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:1</td>
<td>PCl₅</td>
<td>ca. 100</td>
<td>2.3</td>
<td>9.7</td>
<td>1.03</td>
<td>1.5</td>
</tr>
<tr>
<td>20:1</td>
<td>PBr₅</td>
<td>ca. 100</td>
<td>1.8</td>
<td>9.7</td>
<td>1.13</td>
<td>1.5</td>
</tr>
<tr>
<td>20:1</td>
<td>Ph₃C[SbCl₆]</td>
<td>na</td>
<td>oligomers</td>
<td>9.7</td>
<td>na</td>
<td>24</td>
</tr>
<tr>
<td>20:1</td>
<td>Ph₃C[PF₆]</td>
<td>80</td>
<td>1.6</td>
<td>9.7</td>
<td>1.08</td>
<td>3.5</td>
</tr>
<tr>
<td>20:1</td>
<td>SbCl₅</td>
<td>ca. 100</td>
<td>1.8</td>
<td>9.7</td>
<td>1.11</td>
<td>1.5</td>
</tr>
<tr>
<td>20:1</td>
<td>VCl₄ᵇ</td>
<td>75</td>
<td>0.6</td>
<td>9.7</td>
<td>1.23</td>
<td>4</td>
</tr>
</tbody>
</table>

ᵃYields determined by ³¹P NMR integration. ᵇReaction performed in refluxing CH₂Cl₂.
ᶜCalculated from the initial ratio of monomer to PCl₅ initiator.
Table IV  Effects of Temperature on the Solution Polymerization of Cl₃P=NSiMe₃ (1).

<table>
<thead>
<tr>
<th>M:I (I: PCl₅)</th>
<th>Temperature (°C)</th>
<th>% Yield ²</th>
<th>Reaction Time (min)</th>
<th>Mₙ x 10⁻³ Found</th>
<th>Mₙ x 10⁻³ Calculated⁵</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>20:1</td>
<td>15</td>
<td>ca. 100</td>
<td>120</td>
<td>24.5</td>
<td>9.7</td>
<td>1.06</td>
</tr>
<tr>
<td>20:1</td>
<td>25</td>
<td>ca. 100</td>
<td>60</td>
<td>23.8</td>
<td>9.7</td>
<td>1.05</td>
</tr>
<tr>
<td>20:1</td>
<td>30</td>
<td>ca. 100</td>
<td>40</td>
<td>22.8</td>
<td>9.7</td>
<td>1.01</td>
</tr>
<tr>
<td>20:1</td>
<td>35</td>
<td>ca. 100</td>
<td>35</td>
<td>21.8</td>
<td>9.7</td>
<td>1.01</td>
</tr>
</tbody>
</table>

²Yields determined by ³¹P NMR integration.

⁵Calculated from the initial ratio of monomer to PCl₅ initiator.
Table V  Controlled Endcapping of the Ambient Temperature Solution Polymerization of Cl₃P=NSiMe₃ (1).<sup>a</sup>

<table>
<thead>
<tr>
<th>Time (h)</th>
<th>1/[N=PCl₂]&lt;sub&gt;n&lt;/sub&gt; %</th>
<th>Mₙ x10⁻⁴ Found</th>
<th>Mₙ x10⁻⁴ Calculated&lt;sup&gt;b&lt;/sup&gt;</th>
<th>(PDI)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.25</td>
<td>70/30</td>
<td>2.6</td>
<td>-</td>
<td>1.06</td>
</tr>
<tr>
<td>2.5</td>
<td>36/64</td>
<td>3.2</td>
<td>-</td>
<td>1.05</td>
</tr>
<tr>
<td>3.75</td>
<td>5/95</td>
<td>3.8</td>
<td>-</td>
<td>1.03</td>
</tr>
<tr>
<td>24</td>
<td>0/100</td>
<td>4.0</td>
<td>2.4</td>
<td>1.02</td>
</tr>
</tbody>
</table>

<sup>a</sup> All polymerizations were carried out with a monomer to initiator ratio of 50:1. See Experimental Section for details.

<sup>b</sup>Calculated from the initial ratio of monomer to PCl5 initiator.
Figure 1. GPC Chromatograms for the Controlled End-Capping of a PCl5-Induced Polymerization of 1 with (CF₃CH₂O)₃P=NSiMe₃. At a) T = 1.25 h, b) T = 3.75 h, and c) 24 h.
Figure 2. $^{31}$P NMR Spectrum of the Controlled Endcapping of $[N=PCl_2]_n$ with $Me_2(CF_3CH_2O)P=NSiMe_3$. 
Figure 3. Molecular weight vs. time for a 46:1 1:PCl₅ reaction.
Figure 4. Kinetics study of 93:1 1:PCl₅ reaction as monitored by $^1$H NMR.
Figure 5. Kinetics study of 93:1 1:PCl₅ reaction as monitored by $^{31}$P NMR.
Figure 6. Evidence for macrocondensation. Top GPC chromatogram is the polymer upon immediate substitution with Na[OCH₂CF₃]. Bottom chromatogram is obtained after the polymer has been stirred in the poly(dichlorophosphazene) form for 20 days and then substituted with Na[OCH₂CF₃].
SCHEME 1

\[
\begin{array}{c}
\text{N}=\text{P} \\
\text{Cl} \\
\text{Cl}
\end{array}_{n} \rightarrow \overset{R^{-}}{\begin{array}{c}
\text{N}=\text{P} \\
\end{array}_{n} \begin{array}{c}
\text{R} \\
\text{R}
\end{array}}
\]

\( R = \text{OR}', \text{NHR}', \text{NR}'\text{R}'' \)
SCHEME 2 - PROPOSED MECHANISMS OF POLYMERIZATION

\[
\begin{align*}
\text{Cl} & \quad \text{Cl} \\
\text{Cl} & \quad \text{P} \equiv \text{NSiMe}_3 \\
\text{Cl} & \quad \text{Cl}
\end{align*}
\]

Trace $\text{PCl}_5/\text{CH}_2\text{Cl}_2$  
Trace $\text{Ph}_3\text{C}^+\text{[PF}_6\text{]}^-/\text{CH}_2\text{Cl}_2$

\[
\begin{align*}
\{ \text{Cl}_3\text{P} \equiv \text{N} \rightarrow & \text{PCl}_3^+ \} \text{ PCl}_6^- \\
n \text{Cl}_3\text{P}=\text{NSiMe}_3 \downarrow \\
\{ \text{Cl}_3\text{P} \equiv & \text{N} \} \\
n \text{Cl}_3\text{P}=\text{NSiMe}_3 \downarrow
\end{align*}
\]

\[
\begin{align*}
\{ \text{Cl}_3\text{P} = & \text{N} \rightarrow \text{PCl}_2 \equiv \text{N} \rightarrow \text{PCl}_3^+ \} \text{ PCl}_6^- \\
\{ \text{Cl}_3\text{P} = & \text{N} \rightarrow \text{PCl}_2 \equiv \text{N} \rightarrow \text{PCl}_2 = \text{N}^+ \} \text{ PCl}_6^-
\end{align*}
\]
Scheme 3
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