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

Harry R. Allcock,* Chester A. Crane, Christopher T. Morrissey, James M. Nelson, and Scott D. Reeves

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Charles H. Honeyman and Ian Manners*

Department of Chemistry, University of Toronto, 80 St. George Street, Toronto, Ontario M5S 1A1, Canada

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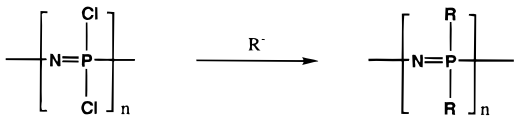
ABSTRACT: A new method for the synthesis of poly(dichlorophosphazene) at ambient temperatures is described. It involves the initiation of $Cl_3P{=}NSiMe_3$ with small amounts of PCl_5 in CH_2Cl_2 to yield poly(dichlorophosphazene), $(NPCl_2)_n$, with narrow polydispersities. The molecular weight of poly(dichlorophosphazene) 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 ^{31}P 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 $Me_2(CF_3CH_2O)P{=}NSiMe_3$ or $(CF_3CH_2O)_3P{=}NSiMe_3$. Furthermore, PBr_5, $SbCl_5$, and $Ph_3C[PF_6]$ were also found to be effective initiators in CH_2Cl_2 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 hexachlorocyclotriphosphazene, $(N{=}PCl_2)_3$, 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 $Cl_3P{=}NP(O)Cl_2$. 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] 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,[6,7] which gives polymers with $M_n \sim 10^5$ and with polydispersity indices of 1.5−3.0. Matyjaszewski and coworkers[8] 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 1.2−2.5.

Scheme 1. Macromolecular Substitution



R = OR', NHR', NR'R"

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.[9] 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,[10] 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.[11]

Results and Discussion

The phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) is known to react with 2 equiv of PCl_5 to form $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$

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with the elimination of Me_3SiCl.[10,12] This ionic species will then interact with an additional equivalent of **1** to eliminate Me_3SiCl and form the short chain cationic species $[Cl_3P{=}NPCl_2{=}NPCl_3]^+[PCl_6]^-$. 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 $Cl_3P{=}NSiMe_3$ (1). (i) Synthesis and Purification. Compound **1** was synthesized initially from $LiN(SiMe_3)_2$ and PCl_5 in hexane at −78 °C. A major challenge was the need to obtain **1** with high purity. The monomer formed by this route did not polymerize in a reproducible manner when treated with trace amounts of PCl_5 in CH_2Cl_2. ^1H NMR spectra and mass spectrometry (CI-MS) revealed the presence of $(Me_3Si)_2NCl$ as a side product. This species appears to inhibit polymerization. Multiple distillations did not remove $(Me_3Si)_2NCl$ because this compound distills at a similar temperature and pressure to **1**. Pure **1** was obtained by treatment of the mixture with PPh_3 (in an excess or stoichiometric amount relative to $(Me_3Si)_2NCl$) in CH_2Cl_2 to form $Ph_3P{=}NSiMe_3$ and Me_3SiCl.[13] 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 PCl_5 with $N(SiMe_3)_3$ in hexane at −78 °C. Although this synthesis generated no $(Me_3Si)_2NCl$ 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.[14]

(ii) Bulk Polymerization of $Cl_3P{=}NSiMe_3$ (1). The addition of small amounts of PCl_5 (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 Me_3SiCl. A ^{31}P 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 with trifluoroethoxy groups and generate a hydrolytically stable derivative, and the resultant species yielded a ^{31}P NMR signal (−6.9 ppm) characteristic of the well-known polymer $[N{=}P(OCH_2CF_3)_2]_n$ (**2**). Analysis of **2** by gel permeation chromatography (GPC) indicated that it possessed a high molecular weight fraction only, with $M_n = 1.2 \times 10^5$ and a polydispersity index (PDI = M_w/M_n) 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 PCl_5, 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 $Cl_3P{=}NSiMe_3$ (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 PCl_5. 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 PCl_5 were monitored by ^{31}P NMR spectroscopy. Only in CH_2Cl_2 or cyclohexane did the polymerizations proceed quantitatively without side reactions. The polymerization in CH_2Cl_2 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 CH_2Cl_2 than in cyclohexane because of the higher polarity, dielectric strength, and solvating ability of CH_2Cl_2. 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 1). Also, in the solution polymerization of **1** in CH_3CN or CH_3NO_2, the poly(dichlorophosphazene) was not completely soluble. The presence of suitable donor solvents may accelerate the reaction by causing greater ion pair separation.

Table 1. Solvent Effects on the Ambient Temperature Solution Polymerization of $Cl_3P{=}NSiMe_3$ (1)

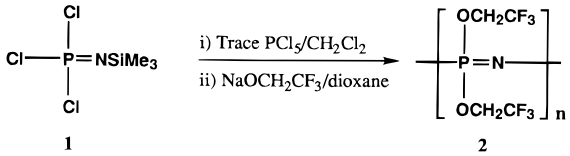
M:I	solvent	% yield polymer[a]	$M_n \times 10^{-4}$ found	$M_n \times 10^{-4}$ calculated[b]	reaction time h	PDI
50:1	CH_2Cl_2	ca. 100	4.2	2.4	4	1.18
50:1	cyclohexane	ca. 100	3.3	2.4	24	1.06
50:1	THF	72	4.4	2.4	48	1.15
50:1	CH_3CN	50	5.3	2.4	48	<1.20
50:1	CH_3NO_2	50	2.0	2.4	48	<1.20

[a] Yields determined by ^{31}P NMR integration. [b] Calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion.

Table 2. Effect of Monomer to Initiator Ratio on the Molecular Weight Polymerization of $Cl_3P{=}NSiMe_3$ (1)[a]

M:I	$M_n \times 10^{-3}$ found[b]	$M_n \times 10^{-3}$ calculated[c]	PDI
4.6:1	5.8	2.5	1.20
9.3:1	10.6	5.0	1.04
23:1	20.2	12	1.09
46:1	53.0	24	1.32
70:1	66.4	36	1.25

[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 at 100% conversion.



1 **2**

However, the reaction of **1** with small amounts of PCl_5 in CH_2Cl_2 resulted in a quantitative conversion to poly(dichlorophosphazene) as estimated by ^1H and ^{31}P NMR spectroscopy and by GPC analysis of the trifluoroethoxy derivative **2**. Polydispersity indices ≤1.32 were obtained. An increase in the ratio of phosphoranimine to PCl_5 in solution brought about an increase in the molecular weight (see Table 2).

The calculated molecular weights shown in Table 2 were predicted on the basis of monomer to initiator ratios, and these differed from the values determined by 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.[15,16] Molecular weights of short chain polymers and oligomers obtained by ^{31}P NMR

Table 3. Effect of Initiator on the Ambient Temperature Solution Polymerization of $Cl_3P{=}NSiMe_3$ (1)

M:I	initiator	% yield **2**[a]	$M_n \times 10^{-4}$ found	$M_n \times 10^{-4}$ calculated[c]	PDI	reaction time (h)
20:1	PCl_5	ca. 100	2.3	0.97	1.03	1.5
20:1	PBr_5	ca. 100	1.8	0.97	1.13	1.5
20:1	$Ph_3C[SbCl_6]$	na	oligomers	0.48	na	24
20:1	$Ph_3C[PF_6]$	80	1.6	0.48	1.08	3.5
20:1	$SbCl_5$	ca. 100	1.8	0.97	1.11	1.5
20:1	VCl_4[b]	75	0.6	0.97	1.23	4

[a] Yields determined by ^{31}P NMR integration. [b] Reaction performed in refluxing CH_2Cl_2. [c] Calculated from the initial ratio of monomer to initiator at 100% conversion.

spectroscopy based on the end group to middle unit ratios correspond more closely to the expected values. Although the growing polymer chains are expressed as $[Cl(PCl_2{=}N)_nPCl_3]^+[PCl_6]^-$, which implies localized alternating single and double bonds, previous ^{31}P NMR spectroscopy[17–19] and X-ray[20] crystallographic data indicate that the charge is not localized at one end of the chain, but delocalized throughout the chain. Therefore, the PCl_3 groups on each end of the growing polymer chains have a single chemical shift by ^{31}P NMR. For example, a ^{31}P NMR spectrum of a 20:1 **1**:PCl_5 ratio sample contained small peaks at 9 ppm (d, PCl_3 terminal), −14 ppm (t, PCl_2PCl_3), and −15 ppm (t, PCl_2-PCl_2PCl_3), along with an intense peak at −17 ppm (br, s, $-(PCl_2)_n-$), characteristic of the known resonance for the middle units of the polymer chain $(N{=}PCl_2)_n$. The peak ratio determined by integration is 1:1:1:17, which corresponds well to the theoretical structure for a 40 repeat unit macromolecule.

(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 3). Phosphorane species such as PX_5 (X = Cl, Br) rapidly initiate the polymerization of **1**. Previous work has shown that the reaction of the phosphoranimine **1** with 2 equiv of PCl_5 results in the formation of $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$.[10,12] Successive additions of 1 and 2 equiv of **1** yield the oligomeric species $[Cl_3P(NPCl_2)_xNPCl_3]^+[PCl_6]^-$, with $x = 2$ and 3, respectively.[10] Reaction of **1** with $PhPCl_4$ in a 10:1 molar ratio produced poly(dichlorophosphazene) which, after treatment with $NaOCH_2CF_3$, was found to possess $M_n = 1.2 \times 10^3$ 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 $SbCl_5$ were also found to be efficient initiators for the polymerization of **1**. For example, in an attempt to compare the reactivity of PCl_5 and $SbCl_5$ toward **1**, two separate samples of **1** were treated with 5% molar equiv of PCl_5 and $SbCl_5$ in CH_2Cl_2. Both reactions proceeded at similar rates and were complete within 1.5 h, as indicated by the disappearance of the ^{31}P NMR resonance for **1** at −54 ppm. After treatment of the resultant $(N{=}PCl_2)_n$ with sodium trifluoroethoxide, the GPC molecular weights and polydispersities for the PCl_5- and $SbCl_5$-induced polymerizations were found to be very similar. The PCl_5-induced polymerization produced $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) with a M_n of 2.3×10^4 (PDI = 1.03) within 1.5 h and the $SbCl_5$-initiated polymerization produced a counterpart with a M_n of 1.8×10^4 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 $TiCl_4$, Cp_2TiCl_2, $TaCl_5$, WCl_6, and VCl_4, and main group Lewis acids, such as dibutylboron triflate ($Bu_2BOSO_2CF_3$), $POCl_3$, $AlCl_3$, Et_2AlCl, $SnCl_4$, and $SnCl_2$, did not initiate the polymerization of **1** at room temperature but instead reacted with $Cl_3P{=}NSiMe_3$ in *refluxing* CH_2Cl_2 to produce macromolecules with lower molecular weights and with polydispersity values higher than those obtained by the ambient temperature route. For example, a 20:1 ratio of **1**:VCl_4 at 60 °C yielded poly(dichlorophosphazene) which, after treatment with $NaOCH_2CF_3$, had a M_n of 6.0×10^3 (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 manner to the formation of the cationic species $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$.[10] Previous phosphoranimine reactivity studies have shown that the phosphoranimine **1** reacts with BX_3,[21] WCl_6,[12] or $TaCl_5$[22] to form stable neutral adducts $Cl_3P{=}NMX_n$ (M = B, $X_n = X_2$; M = W, $X_n = Cl_5$; M = Ta, $X_n = Cl_4$).

Several trityl salts were also found to react with **1** at 25 °C. Reaction of $Ph_3C[PF_6]$ (5 mol %) with **1**, followed by polymerization for 4 h and halogen replacement, yielded **2** in ca. 80% yield ($M_n = 1.6 \times 10^4$; PDI = 1.08), with the remaining 20% consisting of the cyclic species $(N{=}PCl_2)_x$ identified by their ^{31}P NMR resonances (x = 3, 20.8 ppm and $x = 4$, −7.1 ppm, respectively).[23] In a similar experiment **1** was treated with $Ph_3C[SbCl_6]$ (20 mol %) in CH_2Cl_2 and the reaction was monitored by ^{31}P NMR spectroscopy over a 24 h period. The trityl hexachloroantimonate salt produced mainly cyclic species $(N{=}PCl_2)_{3,4}$ and linear oligomers as determined by GPC and ^{31}P 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 $\{Cl_3P{=}N^+\}$, as reported for the high-temperature cationic polymerization of tris(organo)phosphoranimines by Matyjaszewski and coworkers.[8] Such an intermediate in our polymerizations would then interact with further equivalents of **1** via reaction at phosphorus to produce Me_3SiCl and a growing, even-numbered oligomer $(N{=}PCl_2)_n$. This proposed mechanism contrasts with the PCl_5-induced polymerizations in the sense that, with phosphorane catalysts, odd-numbered chains are produced, such as $[(Cl_2P{=}N)_xPCl_3]^+[PCl_6]^-$ (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 $Ph_3C[SbCl_6]$ as an initiator, the trityl salt was reported not to be the active initiator,

Scheme 2. Proposed Mechanism of Polymerization

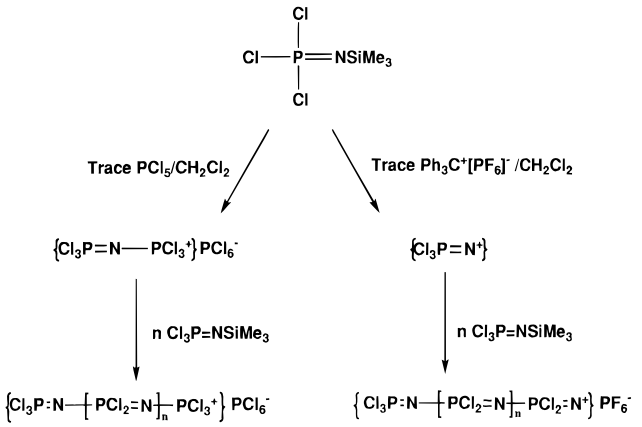


Table 4. Effects of Temperature on the Solution Polymerization of $Cl_3P{=}NSiMe_3$ (1)

M:I (**1**:PCl_5)	temperature (°C)	% yield **2**[a]	reaction time (min)	$M_n \times 10^{-3}$ found	$M_n \times 10^{-3}$ calculated[b]	PDI
20:1	15	ca. 100	120	24.5	9.7	1.06
20:1	25	ca. 100	60	23.8	9.7	1.05
20:1	30	ca. 100	40	22.8	9.7	1.01
20:1	35	ca. 100	35	21.8	9.7	1.01

[a] Yields determined by ^{31}P NMR integration. [b] Calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion.

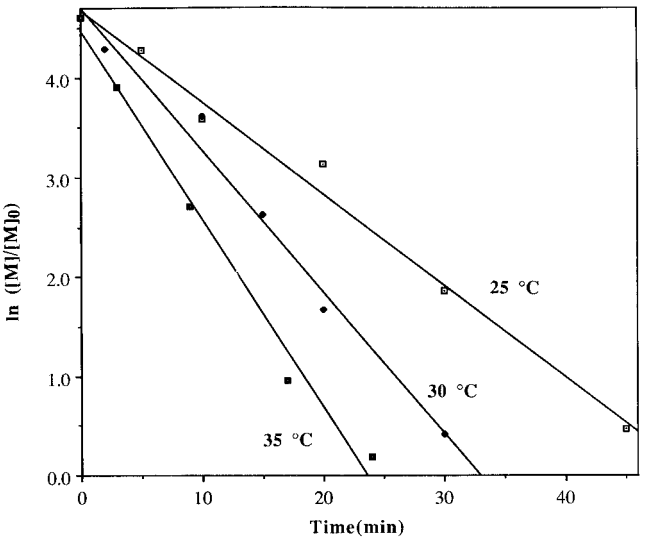


Figure 1. Kinetic study of a 20:1 **1**:PCl_5 reaction in methylene chloride at various temperatures. $[M_0]$ = initial monomer concentration. [M] = monomer concentration at time *t*.

but rather $SbCl_5$ formed through an equilibrium with the hexachloroantimonate salt.[8] Clearly no such equilibrium exists in our ambient temperature polymerizations based on the efficiency of $SbCl_5$-induced polymerizations of **1** mentioned earlier (see Table 3).

(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 PCl_5 in CH_2Cl_2. The polymerizations were monitored by ^1H and ^{31}P NMR spectroscopy from 15 to 35 °C over the course of the polymerization (see Table 4). Lowering of the temperature increased the times needed for completion of the polymerization, while temperature increases decreased the polymerization times.

Plots of $\ln([M]/[M]_o)$ versus time for reactions at 25, 30, and 35 °C were obtained and shown to be linear (see Figure 1). From these plots, the rate constants (k_p) were determined and were shown to follow the Arrhenius equation. From the plot of $\ln(k_p)$ versus inverse temperature, a straight line was obtained (see Figure 2). The plot provided Arrhenius parameters and the activation energy, E_a, was found to be 54.6 kJ/mol, with a pre-exponential factor, *A*, of 2.0×10^9 s^{-1}. The PCl_5-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**:PCl_5 ratio reaction was examined at −50 and 25 °C and was monitored by ^1H and ^{31}P 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 PCl_5 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 ^{31}P 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 1 week while the ratio of **1** to poly(dichlorophosphazene) was monitored by ^{31}P 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 1 h. Thus, at low temperatures, the chain ends appear to be still active after propagation has ceased. This is strong evidence for a living polymerization.

(vi) Activity of the Chains. A solution of poly(dichlorophosphazene) in CH_2Cl_2 was prepared via the

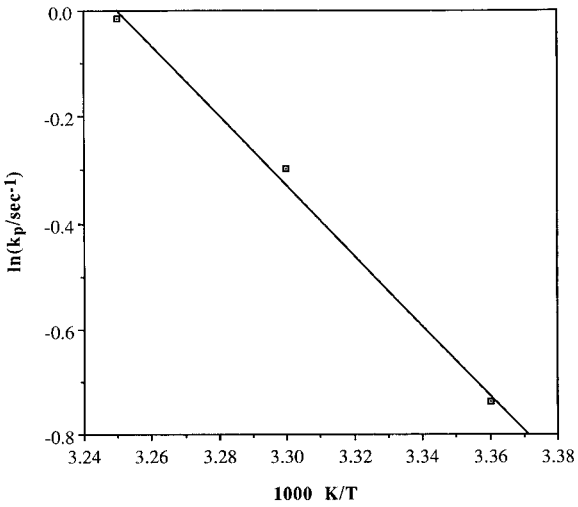


Figure 2. Arrhenius plot for a 20:1 **1**:PCl_5 reaction at various temperatures.

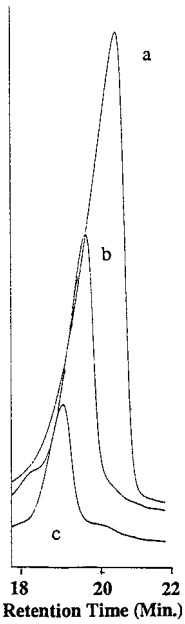


Figure 3. GPC chromatograms for the controlled end-capping of a PCl_5-induced polymerization of **1** with $(CF_3CH_2O)_3P{=}NSiMe_3$ at T = (a) 1.25 h, (b) 3.75 h, and (c) 24 h.

Table 5. Controlled End-Capping of the Ambient Temperature Solution Polymerization of $Cl_3P{=}NSiMe_3$ (1)[a]

		$M_n \times 10^{-4}$		
time (h)	**1**:$[N{=}PCl_2]_n$ %	found	calculated[b]	(PDI)
1.25	30:70	2.6		1.06
3.75	5:95	3.8		1.03
24	0:100	4.0	2.4	1.02

[a] All polymerizations were carried out with a monomer to initiator ratio of 50:1. See Experimental Section for details. [b] Calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion.

reaction of **1** with PCl_5 in a 9.3:1 ratio in which all the phosphoranimine had been converted to polymer, as determined by ^1H and ^{31}P NMR spectroscopy. A portion of this sample was subjected to halogen replacement as described above to yield a trifluoroethoxy-substituted polymer **2** with $M_n = 1.1 \times 10^4$ and PDI = 1.09. Further addition of phosphoranimine to the remaining polymerization mixture to generate a molar ratio of **1**:$(NPCl_2)_n$ 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 $M_n = 4.4 \times 10^4$ 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 reagants, 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 $(CF_3CH_2O)_3P{=}NSiMe_3$,[24] where the presence of the $SiMe_3$ 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 equiv of PCl_5 in CH_2Cl_2, was treated with trace quantities of $(CF_3CH_2O)_3P{=}NSiMe_3$ at regular intervals during the polymerization, the growth of the polymeric cation was quenched as monitored by ^{31}P NMR spectroscopy. GPC examination of the resultant polymers after chlorine replacement with $NaOCH_2CF_3$ showed a consistent range of molecular weights for the end-capped polymerization (see Table 5 and Figure 1). Unfortunately, the presence of the terminal $-N{=}P(OCH_2CF_3)_3$ group in the end-capped polymer could not be confirmed from the ^{31}P NMR spectrum of an oligomeric sample of poly(dichlorophosphazene) synthesized from treatment of **1** with a 20% molar equiv of PCl_5. The resonance for the terminal $-N{=}P(OCH_2CF_3)_3$ species was perhaps concealed by resonances for the oligo(dichlorophosphazene) species. In a further effort to confirm the presence of such end-capping groups, an oligomeric sample of $(N{=}PCl_2)_n$, synthesized by treatment of **1** with a 10% molar equiv of PCl_5, was treated with $Me_2(CF_3CH_2O)P{=}NSiMe_3$.[24] Examination of this end-capped species by ^{31}P NMR spectroscopy revealed the terminal $-N{=}PMe_2(OCH_2CF_3)$ species from a doublet resonance at 9.4 ppm (Figure 4). The M_n of this end-capped oligomer was found to be 5.9×10^3 (PDI = 1.05, by GPC) after macromolecular substitution with $NaOCH_2CF_3$.

(vii) Molecular Weight Changes as a Function of Percent Conversion. The solution polymerization of **1** with a 46:1 monomer:PCl_5 initiator ratio in CH_2Cl_2 was monitored as a function of percent conversion. Aliquots were removed at regular intervals and the chlorine atoms were replaced by treatment with $NaOCH_2CF_3$. 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 percent conversion. This is the situation with this system, as illustrated in Figure 5.

(viii) 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**:PCl_5 sample was monitored with ^1H and ^{31}P NMR spectroscopy. A plot of $\ln([M]/[M]_o)$ versus time (Figures 6 and 7) showed a linear relationship and this suggests pseudo-first-order kinetics. The rate constant (k_p) for the propagation of this polymerization was calculated as $k_{297} = 6.5 \times 10^4\ s^{-1}$.

Based on the above evidence, this polymerization can be characterized as a "living" cationic polymerization. The original Szwarc definition of living polymerization requires that the polymerization follows first-order kinetics with respect to monomer concentration, the number-average degree of polymerization is proportional to the monomer conversion, and the molecular weight distribution corresponds to the Poisson distribution.[25] The system described here meets all three of

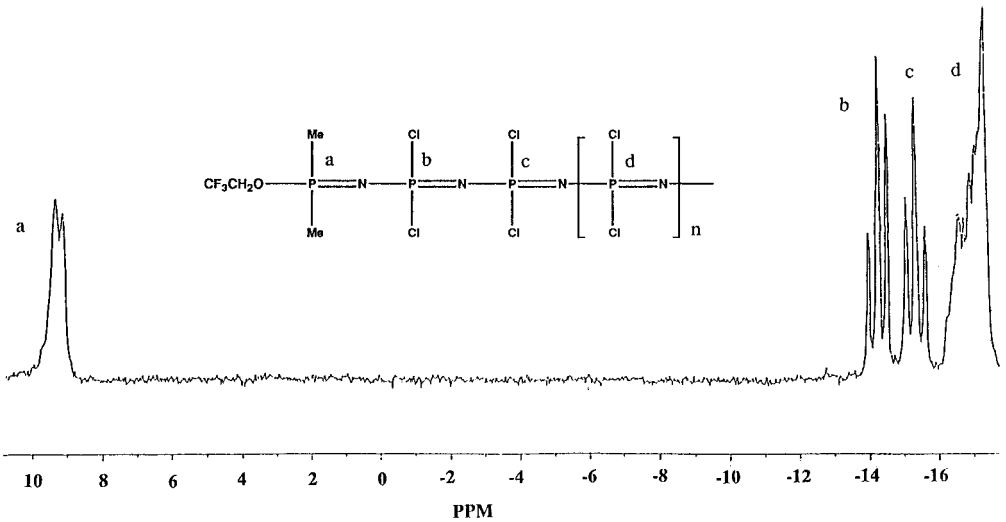


Figure 4. ^{31}P NMR spectrum of the controlled end-capping of $[N{=}PCl_2]_n$ with $Me_2(CF_3CH_2O)P{=}NSiMe_3$.

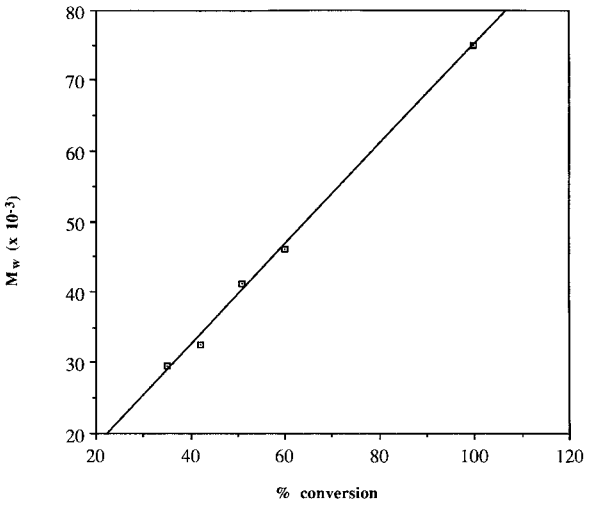


Figure 5. Molecular weight vs percent conversion for a 46:1 **1**:PCl_5 reaction.

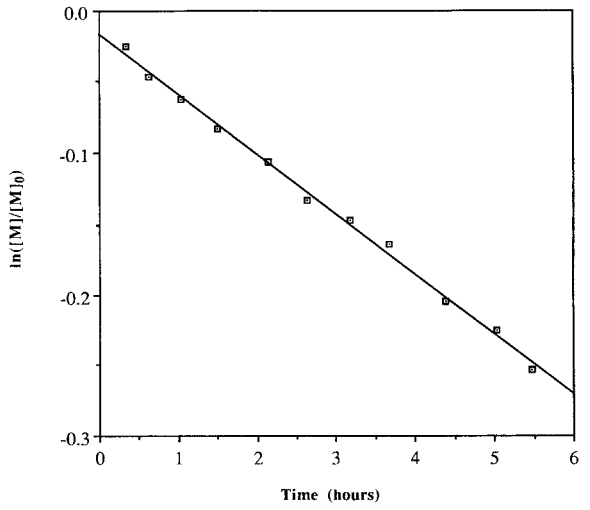


Figure 6. Kinetics study of 93:1 **1**:PCl_5 reaction as monitored by ^{1}H NMR.

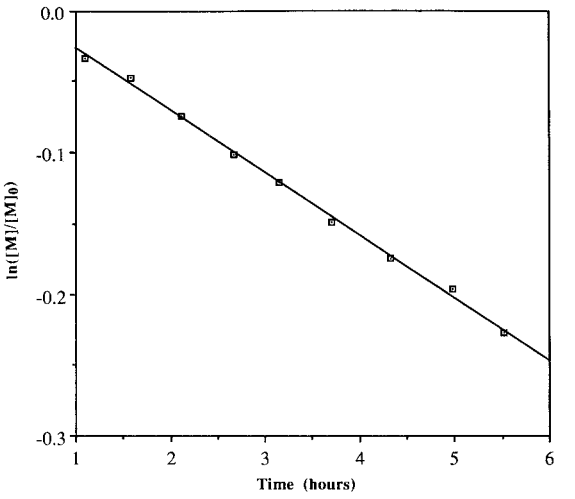


Figure 7. Kinetics study of 93:1 **1**:PCl_5 reaction as monitored by ^{31}P NMR.

these requirements. Furthermore, recent discussions in the literature suggest that classification of living systems be based on the shelf time of the active polymers.[26] This polymer system remains active for at least 24 h after complete conversion of monomer to polymer, which is significantly longer than many organic systems classified as "living".

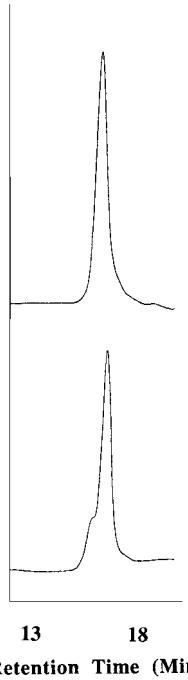
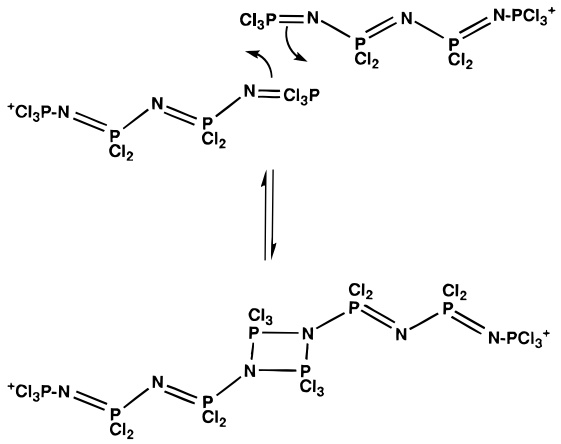


Figure 8. Evidence for macrocondensation. The top GPC chromatogram is the polymer upon immediate substitution with Na[OCH_2CF_3]. The bottom chromatogram is obtained after the polymer has been stirred in the poly(dichlorophosphazene) form for 20 days and then substituted with Na[OCH_2CF_3].

(ix) Evidence for Macrocondensation. Samples of poly(dichlorophosphazene) that were not subjected to halogen replacement immediately following complete conversion to polymer, 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 $NaOCH_2CF_3$ 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 $M_n = 2.0 \times 10^4$ and PDI = 1.09, as seen in Figure 8. The second sample was not substituted but was stirred at 25 °C for 20 days in the $(N{=}PCl_2)_n$ form. It was then treated with $NaOCH_2CF_3$ 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 $(N{=}PCl_2)_n$ 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 ($Cl_3P{=}N-$) 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

Scheme 3. Macrocondensation



complete conversion of monomer or to store the material at temperatures below 0 °C.

(x) High Molecular Weight Polymers. Polymerizations at ratios of **1**:PCl_5 higher than 150:1 in CH_2Cl_2 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: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 ^{31}P 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 1 week (each ca. 25:1 **1**:$[PCl_5]_{initial}$). The resultant polymer was then treated with $NaOCH_2CF_3$ to provide high molecular weight polymer **2** (multimodal GPC trace with peaks at $M_n = 1.2 \times 10^6$, PDI = 1.18; $M_n = 3.7 \times 10^4$, PDI = 1.47; $M_n = 8.8 \times 10^3$, 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 Phophoranimines. The procedures discussed above also allow organic-substituted monomers such as $PhCl_2P{=}NSiMe_3$, $Ph_2ClP{=}NSiMe_3$, $Me(Et)ClP{=}NSiMe_3$, and $(CF_3CH_2O)_2BrP{=}NSiMe_3$ to be polymerized in the same way to give polymers $[N{=}P(Ph)(OCH_2CF_3)]_n$, $[N{=}P(Ph)_2]_n$, $[N{=}PMe(Et)]_n$, and $[N{=}P(OCH_2CF_3)_2]_n$. This aspect has also been developed in detail, and will reported in a forthcoming publication.[27]

Summary. The cationic polymerization of $Cl_3P{=}NSiMe_3$ (**1**), initiated by phosphoranes such as PCl_5, provides access to poly(dichlorophosphazene) with controllable molecular weights and narrow polydispersities. The 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 fundamental development of polyphosphazenes. In addition, the ambient temperature method provides an effective direct route to poly(organophosphazenes) via the PCl_5-induced polymerizations of mono- and diorganosubstituted phosphoranimines. 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, $TiCl_4$, Cp_2TiCl_2, $TaCl_5$, WCl_6, VCl_4, $SbCl_5$, dibutylboron triflate (1 M solution in dichloromethane), $POCl_3$, $AlCl_3$, Et_2AlCl (1.8 M solution in toluene), $SnCl_4$, $SnCl_2$, 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. $PhPCl_4$,[28] sodium trifluoroethoxide,[29] $Me_2(CF_3CH_2O)P{=}NSiMe_3$,[24] and $(CF_3CH_2O)_3PNSiMe_3$[24] 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 CaH_2 and then from P_2O_5 into the reaction flask. Acetonitrile, nitromethane, and cyclohexane (Aldrich) were distilled from P_2O_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 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. ^{29}Si NMR spectra were recorded with use of a Bruker AM-300 NMR operated at 59.6 MHz and were referenced externally to $SiMe_4$. ^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. 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 $Cl_3P{=}NSiMe_3$ (1). Compound **1** was synthesized as reported previously,[12] with the modification that the distilled mixture of **1** and $(Me_3Si)_2NCl$ was treated with PPh_3 (amount as determined by ^1H NMR integration) and the resultant mixture was redistilled at reduced pressure. Yield: 43%. ^1H NMR ($CDCl_3$): $\delta = 0.18$ ppm (d, $^4J_{PH} = 1$ Hz); ^{31}P NMR ($CDCl_3$): $\delta = -54$ ppm. ^{13}C NMR ($CDCl_3$): 1.9 ppm (d, $^4J_{CP}$ 7 Hz, $SiCH_3$); ^{29}Si NMR ($CDCl_3$): $\delta = 0.27$ (d, $^2J_{PSi} = 11$ Hz). MS (CI, 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_2Cl_2 was placed in a Schlenk flask in a glovebox and was stirred with use of a magnetic stirrer. A solution of 0.2 g (0.89 mmol) of **1** in 2 mL of CH_2Cl_2 was then added to the flask. The reaction mixture was monitored by ^1H and ^{31}P NMR spectroscopy. After complete conversion of **1** 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 mmol) in dioxane (4 mL). The mixture was then refluxed for 1 h and stirred at 25 °C for 24 h. The polymer was then precipitated into deionized water (3×) and hexane (2×) (yield: 72%). In order to control the molecular weight, the ratio of monomer to initiator was varied by changing the amount of monomer while all other amounts were kept constant.

(b) For the polymerization study in a variety of solvents, the above procedure was followed. However, 0.21 g of **1** (0.94 mmol) was dissolved in 2.0 mL of solvent followed by the addition of 1.0 mL of 19 mM PCl_5 (0.0192 mmol) in each respective solvent: (i) CH_2Cl_2, (ii) cyclohexane, (iii) THF, (iv) CH_3CN, and (v) CH_3NO_2. In all the polymerizations, the resulting $[N{=}PCl_2]_n$ was treated with $NaOCH_2CF_3$ and was examined by GPC: (i) $M_n = 4.2 \times 10^4$ and PDI = 1.18, (ii) M_n

$= 3.3 \times 10^4$ and PDI = 1.06, (iii) $M_n = 4.4 \times 10^4$ and PDI = 1.15, (iv) $M_n = 5.3 \times 10^4$ and PDI = 1.02 and (v) $M_n = 2.0 \times 10^4$ and PDI = 1.03.

(c) The variable temperature experiments were conducted in a 5 mm NMR tube with D_2O 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 CH_2Cl_2 (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 PCl_5 in CH_2Cl_2 at −78 °C. The mixture was immediately warmed to the appropriate temperature in the NMR spectrometer, and the reactions were monitored by ^{31}P and ^1H NMR spectroscopy. The polymerizations were rapid and complete in (i) 120, (ii) 60, (iii) 40, and (iv) 35 min. Treatment with $NaOCH_2CF_3$ of the resulting poly(dichlorophosphazene) was then followed by characterization by GPC: (i) $M_n = 2.5 \times 10^4$ and PDI = 1.06, (ii) $M_n = 2.4 \times 10^4$ and PDI = 1.05, (iii) $M_n = 2.3 \times 10^4$ and PDI = 1.01, and (iv) $M_n = 2.2 \times 10^4$ 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 PCl_5 (0.1 mL 24 mM) in CH_2Cl_2 was followed by the addition of CH_2Cl_2 (0.9 mL) and PCl_5 (1.0 mL 24 mM) in CH_2Cl_2, respectively.

(d) To a stirred solution of **1** (0.4 g, 1.8 mmol) in CH_2Cl_2 (2 mL) was added a 5% molar equiv of (i) PBr_5 (0.01 g, 0.04 mmol), (ii) $SbCl_5$ (0.01 g, 0.04 mmol), (iii) Ph_3CPF_6 (0.02 g, 0.04 mmol), (iv) Ph_3CSbCl_6 (0.03 g, 0.04 mmol), (v) $POCl_3$ (ca. 0.007 g, 0.04 mmol), (vi) $AlCl_3$ (ca. 0.005 g, 0.04 mmol), (vii) $SnCl_4$ (0.01 g, 0.04 mmol), (viii) $SnCl_2$ (0.007 g, 0.04 mmol), (ix) $TaCl_5$ (0.02 g, 0.04 mmol), (x) VCl_4 (0.008 g, 0.04 mmol), (xi) WCl_6 (0.02 g, 0.04 mmol), (xii) $TiCl_4$ (0.009 g, 0.04 mmol), (xiii) Cp_2TiCl_2 (0.01 g, 0.04 mmol), and (xiv) $Bu_2BOSO_2CF_3$ (40 μL of 1.0 M solution in CH_2Cl_2, 0.04 mmol). In the case of i−iii the polymerizations proceeded rapidly to completion [for i and ii within 1.5 h; 3.5 h for iii] and treatment of the resultant $[N{=}PCl_2]_n$ with $NaOCH_2CF_3$ produced **2**, thus permitting molecular weight determination by GPC.

GPC for **2**: i) $M_n = 1.8 \times 10^4$ and PDI = 1.13, ii) $M_n = 1.8 \times 10^4$ and PDI = 1.11, (iii) $M_n = 1.6 \times 10^4$ and PDI = 1.06. In the case of iv only oligomeric species and cyclic species, $(N{=}PCl_2)_{3,4}$, were produced on the basis of the solubility of the resultant products in hexanes and upon confirmation by ^{31}P NMR and GPC. In the case of v−xiv no polymerization behavior was detected over 48 h when monitored periodically by ^{31}P NMR. In addition, polymerization of **1** with a 15% molar amount of VCl_4 in refluxing CH_2Cl_2 over a span of 4 h produced $[N{=}PCl_2]_n$ which was substituted with $NaOCH_2CF_3$ and was found to possess $M_n = 6.0 \times 10^3$ (PDI = 1.23).

Attempted End-Capping of the PCl_5-Induced Polymerization of 1 with the Phosphoranimine Species $(CF_3CH_2O)_3P{=}NSiMe_3$ and $Me_2(CF_3CH_2O)P{=}NSiMe_3$. (a) To a stirred solution of **1** (1.1 g, 4.9 mmol) in 1 mL of CH_2Cl_2 was added a 2% molar equiv of PCl_5 (ca. 0.02 g, 0.1 mmol) at room temperature. At various time intervals, an aliquot of the reaction mixture was treated with $(CF_3CH_2O)_3P{=}NSiMe_3$ (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: $[N{=}PCl_2]_n$:**1** as follows (i) at 1.25 h, 70:30 (GPC: $M_n = 2.6 \times 10^4$ and PDI = 1.06), (ii) at 3.75 h, 95:5 (GPC: $M_n = 3.8 \times 10^4$ and PDI = 1.03), and (iii) at 24 h, 100:0 (GPC: $M_n = 4.0 \times 10^4$ and PDI = 1.02). The relative quantities of $[N{=}PCl_2]_n$:**1** remained consistent over a 24 h period as monitored by ^{31}P NMR spectroscopy**.** The presence of the terminal $-N{=}P(OCH_2CF_3)_3$ 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_2Cl_2 (1 mL) was added a 10% molar equiv of PCl_5 (ca. 0.02, 0.1 mmol) at room temperature. After 30 min. an aliquot of the reaction mixture was quenched with $Me_2(CF_3CH_2O)P{=}NSiMe_3$ (ca. 0.02 g) and was examined immediately by ^{31}P NMR spectroscopy. ^{31}P NMR (CH_2Cl_2): $\delta = 9.4$ (d, $^2J_{PP} = 40$ Hz, $-N{=}PMe_2(OCH_2CF_3)$), −14.2 (t, $^2J_{PP} = 43$ Hz, $-N{=}PCl_2N{=}PMe_2(OCH_2CF_3)$), −15.2 (d, $^2J_{PP} = 40$ Hz, $[-N{=}PCl_2\text{-}N{=}PCl_2\text{-}N{=}PMe_2(OCH_2CF_3)]$) and −16.6 to −17.3 ppm (br s, $[N{=}PCl_2]_n$). Subsequent substitution with $NaOCH_2CF_3$ resulted in the formation of **2**. GPC: $M_n = 5.9 \times 10^3$ and PDI = 1.05.

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