Ambient-Temperature Direct Synthesis of Poly(organophosphazenes) via the "Living" Cationic Polymerization of Organo-Substituted Phosphoranimines

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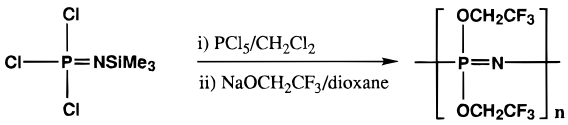
ABSTRACT: A new, ambient-temperature method for the direct synthesis of organo-substituted polyphosphazenes is described. It involves the initiation of a series of organophosphoranimines R(R′)-XP═$NSiMe_3$ (**3**, R = Ph, R′ = X = Cl; **5**, R = R′ = Ph, X = Cl; **7**, R = Me, R′ = Et, X = Cl; **9**, R = R′ = CF_3CH_2O, X = Br) with catalytic amounts of PCl_5 in CH_2Cl_2 to yield (after treatment with $NaOCH_2CF_3$ in the case of **3**) the corresponding polyphosphazene species $(N{=}PRR')_n$ (**4**, R = Ph, R′ = OCH_2CF_3; **6**, R = R′ = Ph; **8**, R = Me, R′ = Et; **10**, R = R′ = OCH_2CF_3) with narrow polydispersities. The molecular weights of the polyphosphazenes were 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. For monomers **7** and **9** optimum polymerization behavior was found to occur at 35 °C in the absence of solvent in the presence of catalytic quantities of PCl_5. These reactions proceeded to 100% completion, while maintaining molecular weight control and narrow polydispersites. In the case of polymers **4**, **8,** and **10**, which were synthesized with a 10:1 monomer to initiator ratio in CH_2Cl_2, the resultant polymers were analyzed by gel permeation chromatography (GPC) (**4**, $M_n = 2.9 \times 10^3$, polydispersity (PDI = M_w/M_n) = 1.07); **8**, $M_n = 2.2 \times 10^3$, PDI = 1.31; **10**, $M_n = 7.8 \times 10^3$, PDI = 1.23). Poly(diphenylphosphazene), $(N{=}PPh_2)_n$ (**6**), was insoluble in common organic solvents and was characterized by magic angle spinning (MAS) solid state ^{31}P NMR spectroscopy. The effects of side group steric bulk, electron-withdrawing or -donating properties, and leaving group types on the ambient-temperature cationic induced polymerizations are discussed.

Introduction

Properties such as elasticity, controllable surface properties, biocompatability, thermooxidative stability, flame retardancy, ionic conductivity, and electro-optical effects are the basis for the growing interest in polyphosphazenes. This, together with their unique fundamental scientific aspects, has stimulated the synthesis and study of more than 700 different phosphazene-based polymers during the last 30 years.[1,2] The most widely used method for the synthesis of organic-substituted polyphosphazenes involves the use of macromolecular substitution reactions to replace the chlorine atoms in poly(dichlorophosphazene), $(N{=}PCl_2)_n$, by organic groups. Poly(dichlorophosphazene) is normally prepared by the thermal ring-opening polymerization of the cyclic trimer, $(N{=}PCl_2)_3$. However, improved methods for the synthesis of poly(organophosphazenes) are of considerable importance to the continued expansion of this field. Current methods do not allow control of the molecular weights or the polydispersities, and this has been a fundamental drawback that has inhibited a broader development of this branch of polymer chemistry.

In 1995, we reported a new method for the synthesis of poly(dichlorophosphazene), a crucial intermediate for the preparation of most polyphosphazenes. This new process involves the reaction of the phosphoranimine $Cl_3P{=}SiMe_3$ (**1**) with small amounts of PCl_5 at 25 °C (Scheme 1).[3] The new approach allows for the ambient-temperature synthesis of poly(dichlorophosphazene), $(N{=}PCl_2)_n$, via a living cationic induced polymerization, with molecular weight control.[4] This moderate-temperature polymerization route provides an efficient method for the production of a wide variety of polyphosphazenes, as well as phosphazene−organic block copolymers. Another group of polymers that are directly accessible via this new method are organo-substituted polyphosphazenes.

Scheme 1



1 **2**

Poly(organophosphazenes), with direct phosphorus−carbon bonds, at present constitute a relatively small group of polyphosphazenes,[5,6] but these are macromolecules with particularly important structures and properties. The most established synthetic route to poly(organophosphazenes) of this type is via the condensation polymerization of *N*-silylphosphoranimines as developed by Neilson and Wisian-Neilson.[5−7] This polymerization proceeds at temperatures near 180−200 °C, to produce a range of poly(aryl/alkylphosphazenes) with molecular weights (M_n) which approach 1×10^5 and with polydispersity indices (PDI) of 1.5−3.0. In addition, Matyjaszewski and co-workers have demonstrated that phosphoranimines, such as $(CF_3CH_2O)_3P{=}NSiMe_3$, undergo both anionic[8,9] and cationic[10] induced polymerizations at temperatures above 100 °C, to yield [N═P(OCH_2-

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$CF_3)_2]_n$ with molecular weights of $(1.0-5.0) \times 10^4$ and with a wide range of polydispersities (1.3−2.5).

Another pathway to this type of polymer is via the thermal ring-opening polymerization of a variety of mono-, bis-, and tris(organo)-substituted cyclotriphosphazenes.[11−13] Cyclic species such as $N_3P_3(R)Cl_5$ (R = Me, Et, *n*-Pr, *n*-Bu, CH_2CMe_3, CH_2SiMe_3, phenyl-*o*-carborane), $N_3P_3(R)_2Cl_4$ (R = Me, Et), and $N_3P_3(R)_3Cl_3$ (R = Me) undergo ring-opening polymerization at temperatures of near 250 °C, to yield the corresponding polyphosphazene species $[N{=}P(R)Cl\text{-}(N{=}PCl_2)_2]_n$, $[(N{=}P(R)Cl)_2N{=}PCl_2]_n$, and $[N{=}P(R)Cl]_n$ but without molecular weight control and with broad polydispersities.[13] The limitation of the ring-opening method is that, with the exception of cyclic species containing a transannular metallocene substituent which introduces a high degree of ring strain,[14−16] most fully-substituted organophosphazene trimers, $(N{=}PR_2)_3$, do not undergo conversion to high polymer, thus precluding the direct synthesis of fully substituted poly(organophosphazenes), $(N{=}PR_2)_n$, by this route.

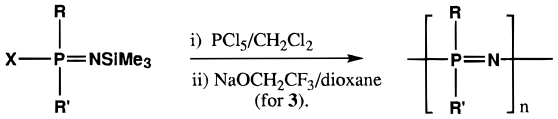
Additional direct routes to poly(organophosphazenes) include the thermal decomposition of phosphine azides, such as Ph(*o*-tolyl)PN_3, which has been employed as a route to $(N{=}PPh(o\text{-tolyl}))_n$.[17,18] This method produces polymers with bimodal molecular weight distributions, in which the higher molecular weight fraction was found to have an M_w of 4×10^4 by GPC analysis.

In this paper, as part of our ongoing study of the scope of the cationic induced ambient-temperature method,[3,4] we report an alternative approach to the direct synthesis of poly(organophosphazenes). These polymerizations take place at ambient temperatures, allow for molecular weight control, and provide polymers with narrow polydispersities.

Results and Discussion

Overall Approach. Initial reactivity studies with the phosphoranimine species $Cl_3P{=}NSiMe_3$ (**1**) revealed that stoichiometric reactions of **1** with PCl_5 produce the short-chain cationic species $[Cl_3P{=}NPCl_3]^+$ $[PCl_6]^-$.[3,19] Addition of small quantities of PCl_5 to **1** resulted in the quantitative formation of poly(dichlorophosphazene), both in solution and in the bulk state.[3] After chlorine replacement with $NaOCH_2CF_3$, these species yielded the hydrolytically stable trifluoroethoxy derivative $[N{=}P(OCH_2CF_3)_2]_n$ (**2**), thus permitting characterization without inadvertent hydrolysis. This improved route to poly(dichlorophosphazene) produces polymers with controlled molecular weights and narrow polydispersities and allows these attributes to be carried through to the derivatives made from this polymer by macromolecular substitution. In view of the existence of a large number of mono- and bis(organo)phosphoranimines,[5,19−25] we have explored the possibility that the "living" cationic, ambient-temperature route can be applied to these monomers also in order to bring about the direct synthesis of poly(organophosphazenes). Our approach has focused on the synthesis of specific phosphoranimine species in order to study the effect of different organic substituents on the PCl_5-induced polymerization. Side groups that provide steric bulk, electron-withdrawing, and electron-donating characteristics have been examined in order to explore the scope of the cationic polymerization method (Scheme 2). A summary of molecular weight data and reaction times for these solution and bulk polymerizations is shown in Tables 1 and 2.

Scheme 2



3: R = Ph; R' = X = Cl
5: R = R' = Ph; X = Cl
7: R = Me; R' = Et; X = Cl
9: R = R' = CF_3CH_2O; X = Br

4: R = Ph; R' = CF_3CH_2O
6: R = R' = Ph
8: R = Me; R' = Et
10: R = R' = CF_3CH_2O

Synthesis and Polymerization of the Phosphoranimines RR′XP=NSiMe₃ (3, R = Ph, R′ = X = Cl; 5, R = R′ = Ph, X = Cl; 7, R = Me, R′ = Et, X = Cl; 9, R = R′ = CF_3CH_2O, X = Br). (*i*) *Synthesis and Polymerization of* $PhCl_2P{=}NSiMe_3$ (**3**). The monophenyl-substituted monomer **3** was synthesized from $LiN(SiMe_3)_2$ and $PhPCl_4$ in hexane at −78 °C[19] in a similar manner to that reported for $Cl_3P{=}NSiMe_3$ (**1**).[3,4] As described previously[4] for the synthesis of **1**, the polymerization inhibitor $(Me_3Si)_2NCl$ was formed as a side product, but monomer **3** could be purified from this impurity by distillation at ca. 50 °C under reduced pressure.

As mentioned in our initial communication,[3] $PhCl_2P{=}NSiMe_3$ (**3**) reacts with small quantities of PCl_5 in the bulk state (without stirring) at 25 °C to yield a macromolecule. The identity of this polymer was confirmed by ^{31}P NMR spectroscopy, which revealed a characteristic resonance at −1.0 ppm for poly[phenyl(chloro)phosphazene], $[N{=}P(Ph)Cl]_n$. After treatment with sodium trifluoroethoxide, this macromolecule was converted to the known polymer $[N{=}P(Ph)(OCH_2CF_3)]_n$ (**4**).[26] Analysis of **4** by gel permeation chromatography (GPC) indicated that it consisted of a high molecular weight fraction only, with an $M_n = 7.1 \times 10^4$ and a polydispersity index (PDI = M_w/M_n) of 1.4 versus polystyrene standards (see Table 2).

The reaction of **3** with PCl_5 was also carried out in CH_2Cl_2 as a solvent. The initial study of the cationic polymerization of **1** in CH_2Cl_2 had revealed that reactions in solution led to decreases in the polydispersity indices compared to polymerizations in the bulk state. Solution polymerizations of **3** were conducted with various monomer to initiator ratios in an effort to obtain molecular weight control in these organophosphazene counterparts. The polymerization of **3** in CH_2Cl_2 proceeded slowly, possibly because of the bulky nature of the phenyl group at phosphorus. A reaction of **3** with PCl_5 in a 10:1 molar ratio in CH_2Cl_2 yielded poly[phenyl(chloro)phosphazene] over a period of 48 h which, after chlorine replacement by treatment with $NaOCH_2CF_3$, produced **4** with an $M_n = 2.9 \times 10^3$ and PDI = 1.07 (see Table 1). Similarly, polymerization of **3** with PCl_5 in a 20:1 molar ratio yielded **4** within 96 h with an $M_n = 1.4 \times 10^4$ and PDI = 1.03, by GPC analysis.

The slowness of the solution polymerization of **3** in CH_2Cl_2 led to a reinvestigation of the bulk polymerization of **3** with PCl_5 *with stirring*, at 25 and 35 °C. These polymerizations proceeded to completion within 8 and 6 h, respectively, accompanied by a significant increase in the viscosity of the reaction mixture. The resultant mixtures were treated with $NaOCH_2CF_3$ to produce the known macromolecule $[N{=}PPh(OCH_2CF_3)]_n$ (**4**) with an $M_n = 1.3 \times 10^4$ (PDI = 1.03, at 25 °C) and $M_n = 1.5 \times 10^4$ (PDI = 1.02, at 35 °C), as determined by GPC analysis. Thus, the PCl_5-induced polymerization of **3** in the bulk state or at 35 °C results in an increased polymerization activity.

Table 1. Polymer Molecular Weights for the PCl_5-Induced Polymerizations of 3, 5, 7, and 9 in CH_2Cl_2

				10^3M_n		
monomer	M:I	% yield	reacn time, h	found	calcd[b]	PDI
3	10:1	90	48	2.9[a]	4.4	1.07
3	20:1	90	96	14.5[a]	5.4	1.03
3	100:1	50	168	16.3[a]	27	1.04
5	10:1	80	48	3.2	3.1	1.01
7	10:1	50	48	2.8	1.8	1.01
9	10:1	80	6	8.4	3.5	1.14

[a] Molecular weights following replacement of Cl by $NaOCH_2CF_3$. [b] Calculated at 100% conversion.

Table 2. Polymer Molecular Weights for the PCl_5-Induced Polymerizations of 3, 7, and 9 under Solvent-Free Conditions

				10^3M_n		
monomer	M:I	% yield	reacn time, h	found	calcd[e]	PDI
3	80:1[a]	90	48	71.1[d]	35.3	1.40
3	10:1[b]	90	8	13[d]	4.4	1.03
3	10:1[c]	90	6	15[d]	4.4	1.02
7	40:1[b]	90	6	5.3	7.1	1.31
7	35:1[c]	85	4	8.8	6.3	1.09
7	50:1[c]	90	4.5	12.2	9.0	1.14
9	10:1[b]	80	6	7.4	3.5	1.23
9	10:1[c]	85	4	9.8	3.5	1.14

[a] Indicates bulk polymerization at 25 °C in sealed ampules, without stirring. [b] Indicates bulk polymerization at 25 °C with stirring. [c] Indicates bulk polymerization at 35 °C with stirring. [d] Molecular weights following replacement of Cl by $NaOCH_2CF_3$. [e] Calculated at 100% conversion.

(*ii) Synthesis and Polymerization of $Ph_2ClP{=}NSiMe_3$ (**5**).* The phosphoranimine $Ph_2ClP{=}NSiMe_3$ (**5**) provided an opportunity to study the effect on the cationic induced polymerization of the additional steric bulk provided by two phenyl groups. This monomer was prepared by similar synthetic methods to those reported for the synthesis of the analogous fluorine derivative, $Ph_2FP{=}NSiMe_3$.[24] Thus, the reaction of Ph_2PCl_3 with $LiN(SiMe_3)_2$ resulted in the formation of **5** in 38% yield.

Monomer **5** was then treated with PCl_5 at 25 °C in a 10:1 ratio, in CH_2Cl_2. The polymerization proceeded very slowly but continued to completion after 48 h, as indicated by the disappearance of the ^{31}P NMR resonance for **5** at 12 ppm. The product was a white solid which was insoluble in a variety of common organic solvents including THF. This precluded molecular weight determination by GPC analysis. Analysis of a THF extract by ^{31}P NMR spectroscopy revealed resonances characteristic of short-chain cationic species, such as $[Ph_2ClP{=}NPCl_3]^+[PCl_6]^-$, based on doublet resonances at 37 and 25 ppm, respectively. These assignments were confirmed by comparison to an authentic sample of $[Ph_2ClP{=}NPCl_3]^+[PCl_6]^-$ synthesized independently via stoichiometric reactions of **5** with 2 equiv of PCl_5 (see Experimental Section for details) in the manner reported previously for the synthesis of $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$.[3] Soxhlet extraction of the insoluble white polymer with hot THF produced a small quantity of a soluble material which was shown by GPC to have an $M_n = 3.2 \times 10^3$ and PDI = 1.01. However, no ^{31}P NMR resonance at approximately −2 ppm was found that corresponded to a species of $[N{=}PPh_2]_n$ (**6**), produced by an alternative method.[27,28]

It is known that some polymeric symmetrically-substituted poly(dialkyl/diarylphosphazenes) are insoluble, particularly the diphenyl- and diethyl-substituted species.[5,6] We reported previously that poly(diphenylphosphazene), synthesized via the macromolecular substitution of $(N{=}PF_2)_n$ with phenyllithium (DP = 200, $M_w = 5.8 \times 10^4$), is soluble enough to allow ^{31}P NMR spectroscopic characterization.[27] However, Matyjaszewski and co-workers have recently mentioned that polymer **6** with a degree of polymerization (DP) higher than 10 is insoluble, presumably due its crystallinity.[17] In an effort to further characterize the target macromolecule **6**, a solid-state MAS ^{31}P NMR was carried out on a sample of **6** synthesized via the reaction of **5** with PCl_5 in a 10:1 ratio. The spectrum of **6** contained multiple resonances centered at ca. 37, 4 to −1, and 24 ppm. Again, these are characteristic of oligomeric cationic species such as $[Cl_3P(N{=}PPh_2)_nPPh_2Cl]^+[PCl_6]^-$. These experiments suggest that the bulky phenyl groups in **5** do not prevent polymerization by the ambient temperature route. However the highly crystalline and insoluble nature of the resultant macromolecular cationic species formed by reaction with PCl_5 reduces the efficiency of the polymerization process.

*(iii) Synthesis and Polymerization of $Me(Et)ClP{=}NSiMe_3$ (**7**).* The unsymmetrical species $Me(Et)ClP{=}NSiMe_3$ (**7**) was prepared to explore the applicability of the PCl_5-induced polymerization to phosphoranimines with two different alkyl groups. The reaction of $EtPCl_2$ with $LiN(SiMe_3)_2$, followed by substitution with MeLi and chlorination with hexachloroethane,[6] produced **7** in 75% yield. The presence of the electron-donating groups in this system also permits a study of the effect of such groups on the cationic induced polymerization.

Monomer **7** was treated with PCl_5 in a 10:1 ratio in CH_2Cl_2 at 25 °C. The polymerization was very slow and did not proceed to completion. ^{31}P NMR spectroscopic analysis of the reaction mixture revealed that, after 48 h of reaction, a resonance at 32 ppm and a broad resonance at 20 ppm existed, and this was consistent with the continued presence of **7** and the known species $[N{=}PMe(Et)]_n$ (**8**),[29] respectively. Examination of **8** by GPC methods showed that this product was in fact a low molecular weight polymer with $M_n = 2.8 \times 10^3$ (PDI = 1.01). The presence of the electron-donating groups probably stabilizes the polymeric cation and inhibits the polymerization. Interestingly, when **7** was treated with PCl_5 in a 40:1 ratio in the bulk phase at 25 °C with stirring, the reaction mixture became very viscous and eventually immobile over a period of 2 h. Examination of the resultant polymerization mixture by ^{31}P NMR spectroscopy and GPC revealed the presence of both unreacted **7** and the slightly higher molecular weight

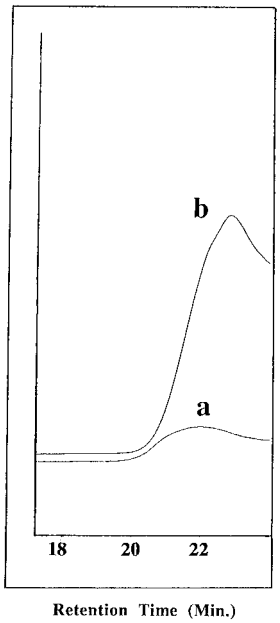


Figure 1. Molecular weight control in the solvent-free polymerization of **7** at 35 °C. GPC chromatograms are shown for $[N{=}PMe(Et)]_n$ (**8**) produced via (a) 35:1 **7**:PCl_5 and (b) 50:1 **7**:PCl_5 ratios.

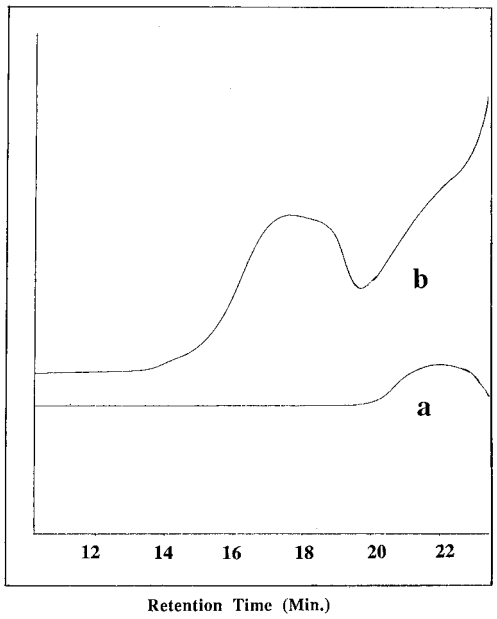


Figure 2. Higher molecular weight polymers in the solvent-free polymerization of **7** at 35 °C. GPC chromatograms are shown for $[N{=}PMe(Et)]_n$ (**8**): (a) With 40:1 **7**:PCl_5; (b) with further addition of **7**.

species **8** with an $M_n = 5.3 \times 10^3$ (PDI = 1.31). The bulk polymerization of **7** at ca. 35 °C was also examined in an effort to study the effect of temperature on the reaction with PCl_5. Reaction of **7** with PCl_5 in a 35:1 ratio proceeded to completion within 4 h to produce polymer **8** with an $M_n = 8.8 \times 10^3$ (PDI = 1.09, by GPC), with no trace of unreacted **7** detectable by ^{31}P NMR spectroscopy. Molecular weight control can be attained in the bulk phase polymerization at 35 °C by variations in monomer to initator ratios (see Table 1 and Figure 1). For example, reaction of **7** with PCl_5 in a 50:1 ratio yielded **8** with an $M_n = 1.2 \times 10^4$ (PDI = 1.09, by GPC).

The growing polymer chains remained active after all the initial monomer **8** had been consumed. A sample of $[N{=}PMe(Et)]_n$ (**8**) was prepared via the reaction of **1** with PCl_5 in a 40:1 ratio under conditions where all the phosphoranimine had been converted to polymer, as determined by ^1H and ^{31}P NMR spectroscopy. A portion of this mixture was shown by GPC to have an $M_n = 1.1 \times 10^4$ and PDI = 1.09. Further addition of phosphoranimine **7** to the remaining polymerization mixture (to generate a molar ratio of **7**:$[N{=}PMe(Et)]_n$ of 5:1) resulted in the continued conversion of **7** to polymer over 24 h. The resultant polymer was only sparingly soluble in THF but dissolved readily in THF which contained ca. 10% H_2O. Similar solubility behavior was reported by Neilson, Wisian-Neilson, and their co-workers for $(N{=}PMe_2)_n$, prepared by their high-temperature condensation route. The GPC analysis of polymer **8** formed from this solution revealed a higher molecular weight component having an $M_n = 9.3 \times 10^4$ and PDI = 1.3 (Figure 2) with a trace of the initial lower molecular weight fraction remaining. Thus, it appears that the active chain ends can resume chain growth following the addition of more monomer, as reported previously for the cationic induced polymerizations of $Cl_3P{=}NSiMe_3$ (**1**).[3,4]

Examination of the ^{13}C NMR spectra of polymer **8** revealed multiple resonances for the carbon atoms attached directly to phosphorus, thus suggesting a lack of stereoregularity in this system. Thus, even the mild nature of the PCl_5-induced, ambient-temperature polymerization apparently does not allow a stereoregular polymer to be formed. Similar conclusions were reported for unsymmetrically substituted polyphosphazenes, such as $[N{=}PMe(Ph)]_n$, produced by the higher temperature condensation polymerization of (Me(Ph)-$(CF_3CH_2O)P{=}NSiMe_3$).[5]

*(iv) Polymerization Behavior of $(CF_3CH_2O)_2BrP{=}NSiMe_3$ (**9**).* The polymerization behavior of the known phosphoranimine $(CF_3CH_2O)_2BrP{=}NSiMe_3$ (**9**)[30] has also been examined. When a sample of **9**, in the absence of solvent, was treated in a 10:1 ratio with PCl_5, polymerization occurred over a 6 h period. The presence of the ^{31}P NMR resonance for $[N{=}P(OCH_2CF_3)_2]_n$ (**10**) at −6.9 ppm was detected. However, the solution polymerization of **9** at 25 °C in CH_2Cl_2 did not proceed to completion. In addition to polymer, the reaction mixture contained unreacted **9**, as revealed by ^{31}P NMR spectroscopy. Analysis of the macromolecule **10** by GPC showed an $M_n = 8.4 \times 10^3$ and PDI = 1.14. Previous work by Wisian-Neilson, Neilson, and co-workers involving the study of the effects of leaving-group variations on the high-temperature condensation polymerization of *N*-silylphosphoranimines, $(CF_3CH_2O)_2XP{=}NSiMe_3$ (X = Cl, Br, OCH_2CF_3), showed that at ca. 100 °C the presence of Me_3SiBr formed via thermal elimination from the initial monomer, and still present in polymerization mixtures, resulted in degradation of the polyphosphazene backbone.[6,31] In our ambient-temperature polymerizations of **9**, efforts were made to terminate the polymerizations after 6−8 h to avoid polymer degradation by Me_3SiBr. Thus, decreased polymerization times and the use of solvent-free conditions were explored in the manner described above for $PhCl_2P{=}NSiMe_3$ (**3**) and $Me(Et)ClP{=}NSiMe_3$ (**7**). Subsequent polymerization of **9** in the bulk phase with PCl_5 in a 10:1 ratio resulted in the formation of **10** within 6 h with $M_n = 7.4 \times 10^3$ and PDI = 1.23, but again unreacted **9** was detected by ^{31}P NMR spectroscopic analysis of the reaction mixture.

The polymerization of **9** in the bulk phase was also examined at ca. 35 °C to determine if an increase in temperature would increase the efficiency of the polym-

erization. Reaction of **9** with PCl_5 in a 35:1 ratio at 35 °C proceeded to completion within 4 h to produce polymer **10** with an $M_n = 9.8 \times 10^4$ (PDI = 1.14, by GPC) and with no trace of unreacted **9** being detectable in the ^{31}P NMR spectrum.

Summary. The PCl_5-induced cationic polymerization of mono- and diorgano-substituted phosphoranimines, RR′XP=$NSiMe_3$ (**3**, **5**, **7**, **9**), at ambient temperatures (ca. 25−35 °C) in solution or in the bulk state, provides an effective direct route to poly(organophosphazenes) with controllable molecular weights and narrow polydispersities. Factors such as side-group steric bulk and the presence of electron-donating side units appear to retard the cationic polymerizations in CH_2Cl_2, but these effects can be overcome by reactions in the absence of a solvent. The polymeric species formed in these reactions remain active after monomer consumption, and this is characteristic of a living polymerization. As a result of our earlier findings about the cationic induced living polymerization of Cl_3P=$NSiMe_3$ (**1**)[3,4] and the series of organophosphoranimines discussed here, we estimate that our system falls between classes 4 and 5, on the basis of Matyjaszewski's classification of "livingness" of polymerizations.[32] Current work in our program is also focused on the synthesis of phosphazene-based copolymers, including the development of phosphazene−organic block copolymers via this ambient temperature route.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide, dichloroethylphosphine, dichlorophenylphosphine, and hexachloroethane were obtained from Aldrich and were used without further purification. Phosphorus pentachloride was also obtained from Aldrich and was sublimed under vacuum. $PhPCl_4$,[33] Ph_2PCl_3,[33] sodium trifluoroethoxide,[34] and $(CF_3CH_2O)_2BrP$=$NSiMe_3$ (**9**)[30] were synthesized and purified by literature procedures. 1,4-Dioxane 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.

All glassware was dried overnight in an oven or was flame-dried under vacuum before use. The reactions were carried out 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 a Bruker WM-360 NMR operated at 146, 90.27, and 360 MHz, respectively. ^{29}Si NMR spectra were recorded on 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. Solid-state magic angle spinning (MAS) ^{31}P NMR was performed with use of a Chem-Magnetics 300 NMR spectrometer operated at 120.5 MHz. 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 guard and AM gel 10 μm linear and AM gel 10 μm 10^4 Å column, with the system 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 $PhCl_2P$=$NSiMe_3$ (3). To a stirred solution of $PhPCl_4$ (21.5 g, 86 mmol) in hexane (200 mL) at −78 °C was added dropwise over 2.5 h a solution of $LiN(SiMe_3)_2$ (14.6 g, 87 mmol) in the same solvent (200 mL). This mixture was stirred at −78 °C for 4 h and was then allowed to warm to room temperature overnight. At this point the supernatant liquid was decanted via cannula and the solvent was removed in vacuo. Distillation of the resultant oil at 53 °C (0.2 mmHg) produced 16.2 g (71%) of **3** as a colorless liquid.

Data for **3**: Yield 55%; ^1H-NMR ($CDCl_3$) δ = 8.0 (dd, $^3J_{HP}$ 19 Hz, $^2J_{HH}(o,m)$ = 8 Hz, 2H, *o*-H), 7.5 (br, 3H, *p*-, *m*-H), 0.2 ppm (d, $^4J_{HP}$ = 3 Hz, 9H, Si−CH_3); ^{13}C-NMR ($CDCl_3$) δ = 133.2 (d, $^4J_{CP}$ = 4 Hz, *p*-Ph), 130.7 (d, $^3J_{CP}$ = 13 Hz *m*-Ph), 128.7 (d, $^2J_{CP}$ = 19 Hz, *o*-Ph), 137.3 (d, J_{CP} = 178 Hz, *ipso*-Ph), 1.9 ppm (d, $^4J_{CP}$ = 7 Hz, Si−CH_3); ^{31}P-NMR (CH_2Cl_2) δ = −11.8 ppm; ^{29}Si ($CDCl_3$) δ = −8.0 ppm (d, $^2J_{PSi}$ = 11 Hz); MS (CI, isobutane) *m*/*z* = 265 (MH^+, 100%), 250 (M^+ − Me, 99%), 230 (M^+ − Cl, 75%) in good agreement with isotopic abundance calculations.

Preparation of Ph_2ClP=$NSiMe_3$ (5). This procedure is based on the reported synthesis of Ph_2FP=$NSiMe_3$.[24] To a stirred solution of Ph_2PCl_3 (20 g, 71 mmol) in hexane (350 mL) at −78 °C was added dropwise a solution of $LiN(SiMe_3)_2$ (11.8 g, 71 mmol) in the same solvent (200 mL). This mixture was stirred at −78 °C for 4 h and was allowed to warm to room temperature overnight. At this point the supernatant liquid was decanted via cannula and the solvent was removed in vacuo. Distillation of the resultant oil at 80 °C (0.2 mmHg) produced 8 g (38%) of **5** as a colorless liquid.

Data for **5**: ^1H-NMR ($CDCl_3$): δ = 8.0 (dd, $^3J_{HP}$ = 18 Hz, $^2J_{HH}$ = 7 Hz, 4H, *o*-,H), 7.5 (m, 6H, *m*-, *p*-H), 0.35 ppm (d , $^4J_{PH}$ = 3 Hz, 9H, $SiMe_3$); ^{13}C-NMR ($CDCl_3$) 136.2 (d, $^2J_{CP}$ = 10 Hz, *ipso*-Ph), 133.3 (d, $^4J_{CP}$ = 6 Hz, *p*-Ph), 130.7 (d, $^3J_{CP}$ = 12, *m*-Ph), 127 ppm (d, $^2J_{CP}$ = 20 Hz, *o*-Ph) 0.4 ppm (d, $^4J_{CP}$ 7 Hz, Si-CH_3); ^{31}P-NMR (CH_2Cl_2) δ = 12 ppm; ^{29}Si ($CDCl_3$) δ = −5.1 ppm (d, $^2J_{PSi}$ = 11 Hz); MS (CI, isobutane) *m*/*z* = 308 (MH^+, 100%), 292 (M^+ − Me, 90%), 272 (M^+ − Cl, 70%) in good agreement with isotopic abundance calculations.

Preparation of Me(Et)ClP=$NSiMe_3$ (7). A hexane suspension of $LiN(SiMe_3)_2$ (31.8 g, 190 mmol) was added dropwise to a solution of $EtPCl_2$ in hexane (25 g, 190 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and was then allowed to warm to room temperature over a 2 h period. The solution was then cooled to −78 °C and 127 mL of 1.5 M MeLi (190 mmol) was added over 1 h, and the mixture was allowed to warm to room temperature. Following solvent removal in vacuo, $Me(Et)PN(SiMe_3)_2$ was isolated and purified by vacuum distillation (70 °C, 80 mmHg). Yield: 25 g (75%). ^{31}P-NMR (CH_2Cl_2): δ = 43.8 ppm. ^1H-NMR ($CDCl_3$): δ = 1.22 (m, 3H, $^2J_{HP}$ = 10 Hz, PCH_3), 0.98 (d, 2H, $^2J_{HP}$ = 14 Hz, PCH_2−), 0.44 (m, $^2J_{PH}$ = 24 Hz, 3H, $-CH_3$) and 0.23 ppm (d, $^4J_{HP}$ = 3 Hz, 9H, Si−CH_3). ^{13}C-NMR ($CDCl_3$): δ = 26.0 (d, $^2J_{CP}$ = 17 Hz, $-CH_3$), 17.4 (d, J_{CP} = 23 Hz, P−CH_2), 9.8 (d, J_{CP} = 20 Hz, P−CH_3) 4.6 ppm (d, $^2J_{CP}$ = 8 Hz, $SiMe_3$).

To a stirred solution of $Me(Et)PN(SiMe_3)_2$ (25 g, 106 mmol) in hexane (200 mL) was added a suspension of hexachloroethane (25.5 g, 106 mmol) in hexane (300 mL) at −78 °C. The reaction mixture was stirred at this temperature for 4 h and was then allowed to warm to room temperature over a 4 h period. Following solvent removal in vacuo, **7** was isolated and purified by vacuum distillation (50 °C, 80 mmHg). Yield: 16 g (75%).

Data for **7**: ^{31}P-NMR (CH_2Cl_2) δ = 32.0 ppm; ^1H-NMR ($CDCl_3$) δ = 1.31 (m, 3H, $^2J_{HP}$ = 10 Hz, PCH_3), 1.09 (d, 2H, $^2J_{HP}$ = 15 Hz, PCH_2−), 0.45 (m, $^2J_{PH}$ = 24 Hz, 3H, $-CH_3$) and 0.27 ppm (d, $^4J_{HP}$ = 3 Hz, 9H, Si−CH_3); ^{13}C-NMR ($CDCl_3$) δ = 32.9 (d, $^2J_{CP}$ = 80 Hz, P−CH_3), 24.4 (d, J_{CP} = 80 Hz, P−CH_2), 6.8 (d, J_{CP} = 5 Hz, $-CH_3$), 2.9 ppm (d, $^2J_{CP}$ = 8 Hz, $SiMe_3$); ^{29}Si ($CDCl_3$) δ = −6.7 (d, $^2J_{PSi}$ = 10 Hz); MS (CI, isobutane) *m*/*z* = 198 (MH^+, 100%), 182 (M^+ − Me, 60%), 162 (M^+ − Cl, 40%) in good agreement with isotopic abundance calculations.

Polymerization of 3, 5, 7, and 9 in Solution. (a) A solution of 0.25 g (0.96 mmol) of **3** in 2 mL of CH_2Cl_2 was treated with PCl_5 (0.02 g, 0.09 mmol) and was stirred at 25 °C. The reaction mixture was monitored by ^1H and ^{31}P NMR spectroscopy over a period of 48 h. After complete consumption of **3**, as evidenced by the disappearance of the ^{31}P NMR resonance for **3** at −12 ppm and the presence of a new resonance at −1.0 ppm for $[N{=}PPh(Cl)]_n$, all volatile species were removed at reduced pressure. The residue 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 to

produce the known macromolecule $[N{=}P(Ph)(OCH_2CF_3)]_n$ (**4**). Polymer **4** was then precipitated into deionized water (3×) and hexane (2×). Data for **4**: Yield 0.2 g (90%); ^{31}P-NMR (CH_2Cl_2) δ = 3.1 ppm;[26] GPC $M_n = 2.9 \times 10^3$ and PDI = 1.07.

The molecular weights of **4** were controlled by variation of the **3**:PCl_5 ratios. Reactions were carried out in 2 mL of CH_2Cl_2 at 25 °C with (i) a 20:1 ratio of **3** (0.50, 1.92 mmol) to PCl_5 (0.02 g, 0.09 mmol) and (ii) a 100:1 ratio of **3** (2.5, 9.6 mmol) to PCl_5 (0.02 g, 0.09 mmol). These reactions were monitored periodically by ^{31}P-NMR spectroscopy. In the case of conditions (i), polymerization was complete within 96 h to give **4** in 90% yield, after chlorine replacement with $NaOCH_2CF_3$. GPC: $M_n = 1.5 \times 10^4$ and PDI = 1.03. In the case of (ii), reaction of **3** with PCl_5 did not proceed to completion during 1 week, based on the presence of **3** (ca. 45−50%) as determined by ^{31}P-NMR spectroscopy. GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.04.

The solution polymerizations of **5**, **7**, and **9** were carried out in a similar manner to that reported for **3** (see above).

(b) Procedure for **5**: Reaction of **5** (0.31 g, 1.0 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in CH_2Cl_2 resulted in the formation of short-chain cationic species similar to $[Ph_2ClP{=}NPCl_3]^+PCl_6^-$ and an insoluble white solid, **6**. Data for $[Ph_2ClP{=}NPCl_3]^+[PCl_6^-]$: ^{31}P-NMR ($CH_2Cl_2$) δ = 37.2 ppm (d, 5.8 Hz, $Ph_2ClP{=}N$), 25.1 (d, 5.8 Hz, N-PCl_3). Data for **6**: Yield 0.15 g (80%); GPC $M_n = 3.2 \times 10^3$ and PDI = 1.01; solid-state MAS ^{31}P NMR δ = 37 for $[Cl_3P(N{=}PPh_2)_nPClPh_2]^+[PCl_6]^-$, 4.0 to −1 for $[Cl_3P(N{=}PPh_2)_nPClPh_2]^+$, and 24 ppm for $[Cl_3P(N{=}PPh_2)_n$-$PClPh_2]^+[PCl_6]^-$.

An authentic sample of $[Ph_2ClP{=}NPCl_3]^+[PCl_6^-]$ was synthesized by reaction of **5** (0.15 g, 0.5 mmol) with 2 equiv of PCl_5 (ca. 0.22 g, 1.1 mmol) in CH_2Cl_2 followed by removal of solvent in vacuo. The resultant product was washed with hexanes and examined by ^{31}P-NMR (CH_2Cl_2): δ = 37.2 ppm (d, 5.8 Hz, $Ph_2ClP{=}N-$), 25.1 (d, 5.8 Hz, $-NPCl_3$).

(c) Procedure for **7**: Treatment of **7** (0.2 g, 1.0 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in a 10:1 ratio, in CH_2Cl_2 , resulted in the slow, incomplete formation of the previously reported polymer, $[N{=}PMe(Et)]_n$ (**8**), over 36 h as monitored by ^{31}P-NMR. Data for **8**: Yield 0.04 g (50%); ^{31}P-NMR (CH_2Cl_2) δ = 20.0 ppm; ^{1}H-NMR ($CDCl_3$) δ = 1.6 (br d, $^3J_{HP}$ = 9 Hz, P−CH_3), 1.45 (br m, $^3J_{HP}$ = 9 Hz, P−CH_2), and 0.95 (br s, $^3J_{HP}$ = 9 Hz, $-CH_3$); ^{13}C-NMR ($CDCl_3$) δ = 29.5−26.4 (m of d, $^2J_{CP}$ = 18 Hz, P−CH_3), 19.2−18.1 (m of d, $^2J_{CP}$ = 18 Hz, P−CH_2), and 5.8 ppm (s, $^2J_{CP}$ = 8 Hz, $-CH_3$); GPC $M_n = 2.8 \times 10^3$ and PDI = 1.01.

(d) Procedure for **9**: Reaction of the known phosphoranimine **9**[30] (0.4 g, 1.0 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in a 10:1 ratio, in CH_2Cl_2, resulted in the incomplete formation of the known macromolecule **10** over 6 h as monitored by ^{31}P-NMR. Data for **10**: ^{31}P-NMR (CH_2Cl_2) δ = −6.9 ppm; GPC $M_n = 8.4 \times 10^3$ and PDI = 1.14.

Solvent-Free Polymerization of 3, 7, and 9. (a) **3** (1.0 g, 3.8 mmol) was placed in a Pyrex tube with 10 mg (0.45 mmol) of PCl_5. The tube was then evacuated (0.1 mmHg) and sealed. After the mixture had been allowed to stand at 25 °C for 48 h, the product had separated into two distinct layers which were examined by ^{31}P-NMR spectroscopy. A ^{31}P-NMR spectrum of the lower layer in THF contained a resonance at −1.0 ppm which was indicative of $[N{=}PPh(Cl)]_n$. This polymeric species was treated with $NaOCH_2CF_3$ in dioxane and was then refluxed for 1 h and stirred at 25 °C for 24 h to produce the known macromolecule $[N{=}PPh(OCH_2CF_3)]_n$ (**4**). Polymer **4** was then precipitated into deionized water (3×) and hexane (2×). Data for **4**: Yield 0.8 g (90%); ^{31}P-NMR (CH_2Cl_2) δ = 3.1 ppm;[26] GPC $M_n = 7.1 \times 10^4$ and PDI = 1.40.

(b) Solvent-free polymerizations of **3** (0.25 g, 0.94 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in a 10:1 ratio were also performed in reaction vials under an inert atmosphere (glovebox), with stirring at 25 and 35 °C. At 25 °C, the reaction of **3** with PCl_5 proceeded to completion within 6 h as monitored by ^{31}P NMR spectroscopy and was accompanied by a significant increase in viscosity. The reaction mixture was treated with $NaOCH_2CF_3$ in dioxane and was stirred at 25 °C for 24 h, to produce the known macromolecule $[N{=}PPh(OCH_2CF_3)]_n$ (**4**). Data for the 25 °C reaction: Yield 0.2 g (90%); ^{31}P-NMR (CH_2Cl_2) δ = 3.1 ppm;[26] GPC $M_n = 1.3 \times 10^4$ and PDI = 1.03. Similarly the 35 °C reaction proceeded efficiently within 6 h, followed by chlorine substitution with $NaOCH_2CF_3$ in dioxane to produce **4**. Data for the 35 °C reaction: Yield 0.2 g (90%); ^{31}P-NMR (CH_2Cl_2) δ = 3.1 ppm;[26] GPC $M_n = 1.5 \times 10^4$ and PDI = 1.02.

The bulk polymerizations of **7** and **9** were carried out in a similar fashion as reported for **3** (see (b), sections (i) and (ii) above).

(c) Reaction of **7** (0.8 g, 4.0 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in a 40:1 ratio at 25 °C resulted in the formation of **8**, accompanied by a significant increase in solution viscosity, which eventually became immobile within 2 h. Examination of the resultant polymerization mixture by ^{31}P-NMR spectroscopy revealed both the presence of unreacted **7** and the polymeric species **8**. Data for $[N{=}PMe(Et)]_n$, (**8**): Yield 0.3 g (90%); GPC $M_n = 5.3 \times 10^3$ and PDI = 1.31; ^{31}P-NMR (CH_2Cl_2) δ = 20.0 ppm.

Reactions were also performed at 35 °C with (i) a 35:1 ratio of **7** (0.66, 3.4 mmol) to PCl_5 (0.02 g, 0.09 mmol) and (ii) a 50:1 ratio of **7** (0.95, 4.8 mmol) to PCl_5 (0.02 g, 0.09 mmol). These reactions were monitored periodically by ^{31}P-NMR spectroscopy. In the case of conditions (i) polymerization was complete within 4 h, as determined by ^{31}P-NMR spectroscopy, to give **8** as an amorphous white solid. Data for (i): Yield 0.26 g (85%); GPC $M_n = 8.8 \times 10^4$ and PDI = 1.09. In the case of conditions (ii) reaction of **7** with PCl_5 also proceeded to completion over the span of 4.5 h, as determined by monitoring of the reaction media by ^{31}P-NMR spectroscopy. Data for (ii): Yield 0.38 g (90%); GPC: $M_n = 1.2 \times 10^4$ and PDI = 1.14.

(d) Reaction of **9**[30] (0.4 g, 1.0 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol), in a 10:1 ratio in the bulk phase, was examined (i) at 25 °C and (ii) at 35 °C. In the case of conditions (i) reaction of **9** with PCl_5 resulted in the formation of **10** within 6 h along with unreacted **9** as determined by ^{31}P-NMR spectroscopic analysis of the reaction mixture. Data for (i): Yield 0.19 g (80%); GPC $M_n = 7.4 \times 10^3$ and PDI = 1.23. In the case of conditions (ii) reaction of **9** with PCl_5 proceeded to completion within 4 h to produce the polymer **10** with no trace of unreacted **9**, as examined by ^{31}P-NMR spectroscopy. Data for (ii): Yield 0.21 g (85%); GPC $M_n = 9.8 \times 10^3$ and PDI = 1.14.

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