Synthesis of Telechelic Polyphosphazenes via the Ambient Temperature Living Cationic Polymerization of Amino Phosphoranimines

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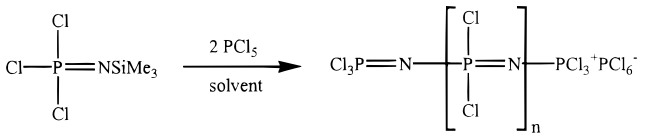
Received March 2, 1999; Revised Manuscript Received June 23, 1999

ABSTRACT: A method for the synthesis of well-defined mono-, di-, and mixed-telechelic polyphosphazenes produced via a living cationic polymerization of phosphoranimines is described. Amino phosphoranimines $R-NH(CF_3CH_2O)_2P{=}NSiMe_3$ (R = Ph−, *p*-BrPh−, *p*-H_3CPh−, $CH_2{=}CHCH_2-$, and $CH_2{=}CHPh-$) were synthesized via a reaction between a bromophosphoranimine and the appropriate organic amine. Ditelechelic polymers $[R-NH]_2-[Cl_2P{=}N]_n$ were prepared by quenching living poly(dichlorophosphazene) chains, $[Cl_3P{=}N(Cl_2P{=}N)_n-PCl_3]^+[PCl_6]^-$ with small quantities of the amino phosphoranimines. Cationic initiators of the amino phosphoranimines were also generated using PCl_5 and were used to polymerize $Cl_3P{=}NSiMe_3$, to give monotelechelic poly(dichlorophosphazenes). In addition, a mixed telechelic system was produced by the termination of an allylamino monotelechelic poly(dichlorophosphazene) chain with a bromoanilino phosphoranimine. In all cases, displacement of the chlorine atoms with sodium trifluoroethoxide yielded hydrolytically stable telechelic polymers with controlled molecular weights and low polydispersities.

Introduction

Polyphosphazenes form one of the largest and most diverse classes of inorganic backbone polymer systems. To date, several hundred different polymers of this type have been synthesized, with a range of physical and chemical properties that rival those of synthetic organic and inorganic macromolecules.[1−4] The fundamental precursor to most polyphosphazenes is poly(dichlorophosphazene), $[Cl_2P{=}N]_n$ (**2**), which undergoes macromolecular substitution with a wide variety of nucleophiles to yield the corresponding derivatized polymers.[5−8] This allows for facile changes to the side group structure which, in turn, permits the modification of bulk and surface properties such as solubility, refractive index, hydrophobicity or hydrophilicity, electrical conductivity, nonlinear optical activity, and glass transition temperatures.[4] Although several synthetic routes exist for obtaining **2**, two general methods are commonly used in our laboratory. The classical approach is a high-temperature ring-opening polymerization of hexachlorocyclotriphosphazene which gives a high molecular weight polymer with a broad polydispersity.[1,2] The second approach is an ambient temperature living cationic induced polymerization of trichlorophosphoranimine (**1**) in the presence of a suitable initiator, such as PCl_5 or $[Cl_3P{=}N-PCl_3]^+[PCl_6]^-$ (Scheme 1). In contrast to the classical approach, this second route provides molecular weight control with narrow polydispersities.[9−13] An extension of this method includes the recent use of the trifunctional cationic species $N-\{CH_2-CH_2NH[(CF_3CH_2O)_2P{=}N-PCl_3]^+[PCl_6]^-\}_3$ to polymerize **1**, thus producing the first star-branched polyphosphazenes.[14] Furthermore, the utility of the cationic living polymerization of $Cl_3P{=}NSiMe_3$ has allowed the production of block copolymers, unattainable via ring-opening polymerization methods. For example, phosphazene−phosphazene block copolymers $[Cl_2P{=}N]_m-[PhClP{=}N]_n$ with different side groups have been synthesized via the stepwise polymerization of monomers such as **1** and $PhCl_2P{=}NSiMe_3$.[13] Replacement of the chlorine atoms with the use of an appropriate nucleophile yields new polymers with tailored properties.

Scheme 1



1 **2**

Until recently, the preparation of block copolymers containing polyphosphazenes has been limited to species with two phosphazene components. A more important objective is the synthesis of macromolecules that contain phosphazene and organic polymer blocks. However, the synthesis of telechelic polyphosphazenes which may be used to couple with preformed organic polymers has proved to be difficult. Nevertheless, the recent use of commercially available organic functionalized polymers such as $MeO-[CH_2CH_2O]_nCH_2CH_2NH_2$ has provided an alternative route to organic−phosphazene block copolymers.[15]

The growing demand for block copolymers with special properties has stimulated a great deal of interest in recent years.[16−20] Access to hybrid copolymers of polyphosphazenes with organic or other inorganic polymers offers a number of advantages relative to their respective homopolymers. The physical, mechanical, and electronic properties of the copolymer can be adjusted in accordance with those of the individual monomeric components. Thus, many of the valuable properties of the respective phosphazene homopolymers, such as thermal and oxidative stability or fire retardance, may be imparted into the copolymer without sacrificing the overall bulk properties.[1,2] Potential applications of such compounds may include uses as nonburning elastomers, flame-retardant foams, or solid polymer electrolytes.

A viable method for the synthesis of block copolymers is through the use of telechelic polymers.[19−22] Telechelic

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10.1021/ma990318f CCC: $18.00 © 1999 American Chemical Society
Published on Web 08/19/1999

polymers have been prepared via free radical and living methods. However, radical methods often yield undesirable features such as branching or high polydispersities.[23] As a result, much of the research on telechelic organic polymers is now based on living anionic polymerization methods which allow for easy end group control.[16,23−28] For instance, the introduction of functional groups via the termination of polystyrene living chain ends has been investigated extensively. These materials can be used either as scaffolds from which monomers can be polymerized or as linking groups which can couple with other preformed polymers to give the corresponding block copolymers.[17,18]

The ability to prepare telechelic polymers from living anionic systems prompted our interest in the generation of similar materials via the living cationic polymerization of phosphoranimines. Previous work has demonstrated that the tris(organo)phosphoranimine species, $(CF_3CH_2O)_3P{=}NSiMe_3$, can be used to quench living cationic chain ends.[10] Thus, it seemed possible that the polymer end group structure could be controlled while introducing additional functionalities via the use of tris(organo)phosphoranimines such as **5a**−**e**. The approach to phosphazene block copolymers described here involves the preparation of end-functionalized materials that are capable of undergoing further reactions. The advantage of employing these materials stems from their versatility in the production of block copolymers, either A−B, A−B−A, or A−B−C, which can be phosphazene−organic or phosphazene−inorganic in nature.

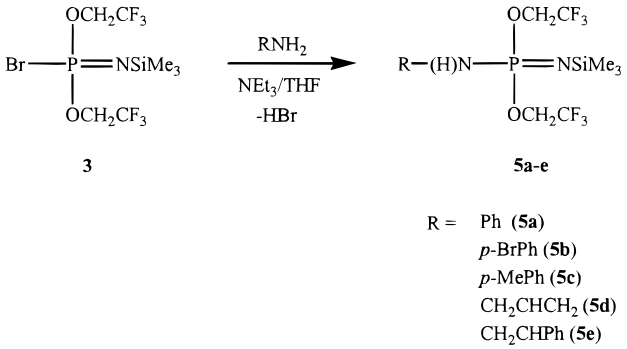
In this paper we report the first telechelic polyphosphazenes synthesized via a living cationic polymerization of phosphoranimines at ambient temperature. Ditelechelic polymers are prepared by utilizing monomers **5a**−**e** as quenching agents for the polymerization process. In addition, the use of short chain cationic initiators, such as $R{-}NH[(CF_3CH_2O)_2P{=}N{-}PCl_3]^+[PCl_6]^-$ (**8a**−**d**), to induce the polymerization of **1** permits the preparation of monotelechelic polymers. Furthermore, the generation of a mixed telechelic polyphosphazene using a combination of the above methods is described.

Results and Discussion

Synthesis of the Functional Phosphoranimines $R{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ (5a−e). Phosphoranimines such as $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**3**) are known to readily undergo bromine replacement reactions in the presence of amines to produce $R{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ species.[29,30] With this in mind, stoichiometric amounts of five different primary amines (R = Ph− (**4a**), *p*-BrPh− (**4b**), *p*-H_3CPh− (**4c**), $CH_2{=}CHCH_2$− (**4d**), and $CH_2{=}CH{-}Ph$− (**4e**)) were allowed to react with **3** in THF and NEt_3 at −78 °C to produce the amino phosphoranimines $R{-}NH(CF_3CH_2O)_2P{=}NSiMe_3$ (**5a**−**e**) (Scheme 2). These products were obtained in good yields after purification by vacuum distillation and were used as initiators and/or terminators in subsequent polymerization reactions.

Aniline (**4a**) was chosen initially as a terminator molecule in order to examine the mechanism of termination and initiation of the living cationic polymerization of **1**. The amino substituents **4b**−**e** were selected because of their functional groups which readily undergo a variety of fundamental organic transformations or polymerizations. For instance, we are currently investigating the coupling of amino-terminated polystyrene with **7b** and **10b** in an attempt to produce polystyrene−phosphazene block copolymers. Similarly, polyphosphazene−siloxane block copolymers are being investigated via hydrosilylation reactions employing **7d** and **10d**.[32] Future possibilities also exist for conducting condensation polymerizations by the conversion of the *p*-tolyl end unit into a reactive carboxylic acid.

Scheme 2



Synthesis of Ditelechelic Polyphosphazenes. As mentioned previously, telechelic polyphosphazenes are attractive precursors for the preparation of block copolymers. In an attempt to produce telechelic polyphosphazenes, the living nature of the cationic polymerization process was investigated. The addition of successive amounts of amino phosphoranimines **5a**−**e** to a living chain of poly(dichlorophosphazene) allowed an examination to be made of the effects this would have on quenching the polymerization. Figure 1a illustrates a typical ^{31}P NMR spectrum which was obtained for a living poly(dichlorophosphazene) chain. The intense peak at −17 ppm (Cl_2P) is characteristic of the middle units of the polymer chain $[N{=}PCl_2]_n$ while the downfield peaks correspond to the terminal PCl_3^+ (d, +8 ppm) as well as the switching groups $PCl_2PCl_3^+$ (t, −14 ppm) and $PCl_2PCl_2PCl_3^+$ (t, −15 ppm). Figure 1b,c indicates the changes that occur when successive amounts of the end cap are added to the reaction mixture. As illustrated, 1 equiv of the amino phosphoranimine (Figure 1b) was not sufficient to terminate the living polymer chain, as indicated by the resonance from the remaining PCl_3^+. Subsequent addition of 1.2 equiv (Figure 1c) of amino phosphoranimine was followed by the disappearance of the PCl_3^+ resonance, and this confirmed that the living polyphosphazene end group had been quenched, thus producing a ditelechelic system. The new resonance that appears between 0 and 1 ppm is attributed to the terminal P−NHR groups which are introduced via end-capping.

This methodology also allowed the controlled introduction of two terminal units onto the polymer chain.[19] Scheme 3 outlines the general reaction sequence employed for the preparation of ditelechelic polymers **7a**−**e**. The length of the polyphosphazene chain was controlled by the ratio of $Cl_3P{=}NSiMe_3$ to PCl_5 in the initial step of the reaction. In all instances, the polymers were isolated in good yield after substitution of the halogen atoms with sodium trifluoroethoxide. It should be noted that all phosphorus atoms are in the P(V) state following substitution with sodium trifluoroethoxide; thus, a third CF_3CH_2O group is substituted onto one of the terminal phosphorus atoms of the polymer. In all instances, the low molecular weight polymers were isolated as adhesive solids; however, they became more crystalline as the length of the polymer chain increased.

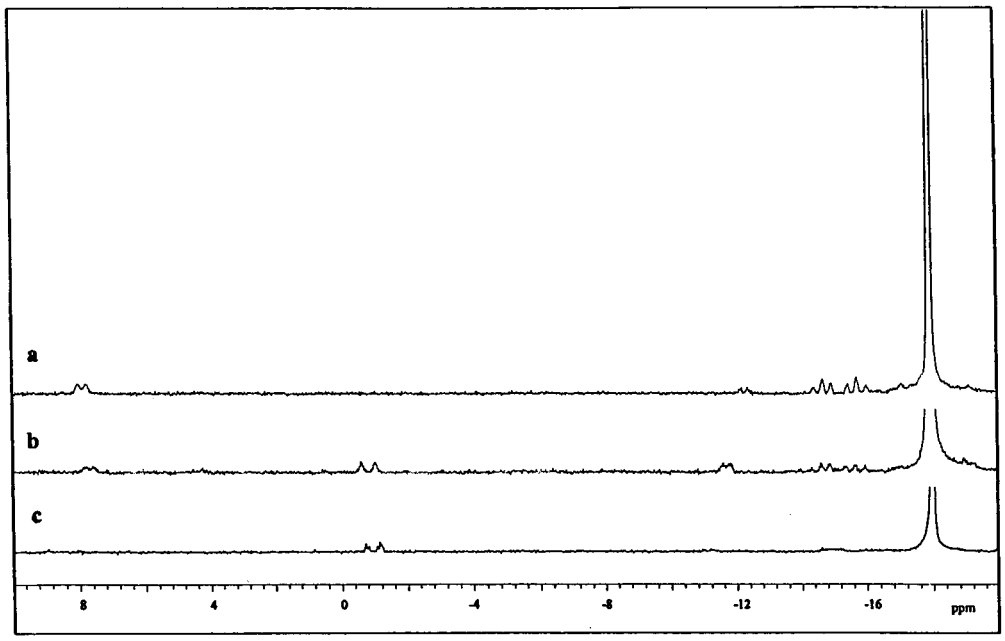
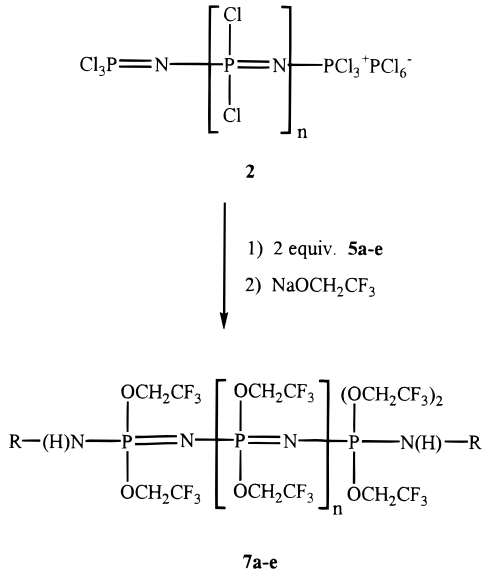


Figure 1. ^{31}P NMR spectrum for (a) a living poly(dichlorophosphazene) chain. (b) One equivalent of amino phosphoranimine end cap added to living polymer. (c) Slight excess of amino phosphoranimine end cap added to quench the polymerization process.

Scheme 3



Characterization of the polymers was performed using multinuclear NMR, gel permeation chromatography (GPC), and MALDI mass spectrometry. Both ^{1}H and ^{13}C NMR were utilized to detect the presence of the new end groups and disappearance of the trimethylsilyl group from the amino phosphoranimine. In all cases, the end groups were detected in the ^{1}H spectrum. However, as the length of the polymer chain increased, their detection via ^{13}C NMR became difficult and sometimes impossible. The molecular weights of these polymers, as determined by gel permeation chromatography, are listed in Table 1. The polymers had low polydispersities across a wide range of molecular weights, which increased with an increased monomer-to-initiator ratio. Figure 2 illustrates the GPC chromatograms for polymer **7b** which show the change in molecular weight as the ratio of **1** to short chain initiator (**6b**) was varied. The low polydispersities obtained for these materials is attributed to the living nature of the polymerization process, while the discrepancy between the calculated GPC molecular weights may be due to an overestimation of molecular weight by GPC.[33]

Table 1. Molecular Weight Data for Ditelechelic Polymers

			$M_n \times 10^{-4}$		
polymer	solvent	M:I	found[a]	calcd[b]	PDI
7a	CH_2Cl_2	50:1	3.69	2.50	1.06
7b	CH_2Cl_2	10:1	1.22	0.57	1.10
7b	CH_2Cl_2	20:1	1.52	1.05	1.09
7b	CH_2Cl_2	25:1	1.64	1.30	1.06
7b	CH_2Cl_2	30:1	2.19	1.54	1.09
7b	CH_2Cl_2	40:1	2.79	2.03	1.13
7b	CH_2Cl_2	60:1	3.75	3.00	1.12
7c	toluene	14:1	1.05	0.75	1.12
7c	toluene	20:1	1.47	1.04	1.16
7c	toluene	40:1	2.52	2.01	1.19
7c	toluene	60:1	4.51	2.99	1.08
7d	CH_2Cl_2	5:1	0.55	0.30	1.37
7d	CH_2Cl_2	10:1	0.98	0.55	1.05
7d	CH_2Cl_2	20:1	1.99	1.03	1.22
7d	CH_2Cl_2	40:1	3.87	2.00	1.08
7e	CH_2Cl_2	20:1	1.59	1.04	1.14
7e	CH_2Cl_2	40:1	2.91	2.02	1.08
7e	CH_2Cl_2	60:1	4.43	2.99	1.18
7e	CH_2Cl_2	80:1	6.10	3.96	1.08

[a] Obtained by GPC vs polystyrene standards. [b] Calculated from the initial ratio of monomer to PCl_5 initiator at 100% conversion.

MALDI mass spectroscopy was also performed on representative samples of these new materials. The MALDI spectrum of a nontelechelic $CF_3CH_2O-[(CF_3CH_2O)_2P{=}N]_n-P-(OCH_2CF_3)_4$ polymer is shown in Figure 3a. The series of signals corresponds to the mass of a $CF_3CH_2O-[(CF_3CH_2O)_2P{=}N]_n-P-(OCH_2CF_3)_4$ polymer as well as a sodium cation (from the matrix). For example, the signal at mass 4681 corresponds to $[(CF_3CH_2O)_2P{=}N]_{17}$ (mass 4131), the CF_3CH_2O and $-P-(OCH_2CF_3)_4$ end groups (mass 527), and a sodium cation (mass 23). The distance calculated between the peaks is assigned to that of a $[(CF_3CH_2O)_2P{=}N]_n$ repeat unit (243 g/mol). A comparison spectrum for end-functionalized polymer **7d** is shown in Figure 3b, which reveals a mass difference of 86 amu between the signals obtained for a polymer of similar repeat unit. In this

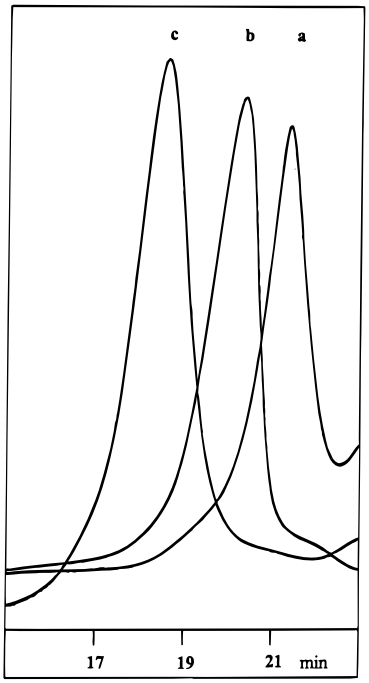


Figure 2. Comparative GPCs for ditelechelic polymers **7b** obtained from monomer (**1**) to PCl_5 ratios of (a) 10:1, (b) 30:1, and (c) 60:1.

spectrum, the signal at 4592 also corresponds to n = 17, plus the $H_2C{=}CHCH_2N(H)$ and $-P-(OCH_2CF_3)_3$ $HNCH_2CH{=}CH_2$ end groups (mass 440) and a sodium cation. This difference in mass of the nontelechelic polymer and **7b** is thus due to the difference in the weight of the end groups (mass 269) which corresponds to the presence of two $H_2C{=}CHCH_2N(H)$ end groups on the ditelechelic polymer chain as opposed to two CF_3-CH_2O end groups. This supports the evidence that the polymer chains are indeed ditelechelic in nature.

Synthesis of Monotelechelic Polyphosphazenes. Monotelechelic materials are important for the future production of diblock copolymers with high certainty.[19] Initial attempts to prepare monotelechelic polymers through the addition of 1 equiv of **5a**−**e** to a living poly(dichlorophosphazene) chain were not successful. This was due to the formation of a mixture of mono- and ditelechelics and homopolymer, which resulted in the production of materials with broad molecular weight distributions. On the basis of these results, an alternative synthetic method for the production of monotelechelic polyphosphazenes was employed. This method is an extension of the previously reported production of di- and triblock poly(ethylene oxide)−polyphosphazene copolymers.[15]

Scheme 4 outlines the strategy used for the production of monotelechelic polyphosphazenes. The amino phosphoranimines (**5a**−**d**) were first initiated with 2 molar equiv of PCl_5 at −78 °C in CH_2Cl_2 or toluene to generate the cationic species $R-NH[(CF_3CH_2O)_2P{=}N-PCl_3]^+[PCl_6]^-$ (**8a**−**d**). The formation of these species was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum for the $N-PCl_3^+$ and $(CF_3CH_2O)_2P{=}N$ units. Subsequent reaction of these initiators with a given amount of $Cl_3P{=}NSiMe_3$ (**1**) allowed the preparation of monotelechelic poly(dichlorophosphazenes) with specific chain lengths. The progress of the reaction was monitored by ^{31}P NMR spectroscopy, and it was found that all polymerizations were complete within 24 h. Integration of the ^{31}P NMR resonances associated with the polymer was consistent with theoretical values. Hydrolytically stable monotelechelic polyphosphazenes (**10a**−**d**) were obtained after macromolecular substitution of the chlorine atoms with sodium trifluoroethoxide. Once again, all the new materials were characterized by spectroscopic and analytical methods. Molecular weights obtained from GPC versus polystyrene standards spanned the range of 0.41−4.53 × 10^4 (Table 2). The amino phosphoranimine **5e** was not used as a short chain cationic initiator due to adverse reactions that occurred when PCl_5 was added to this material. It is believed that the styrene component of the phosphoranimine may also have reacted with the PCl_5, thereby preventing the isolation of the desired initiator molecule.

Scheme 4

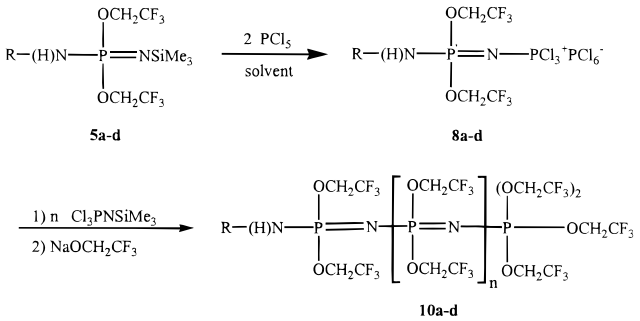


Table 2. Molecular Weight Data for Monotelechelic Polymers

			$M_n \times 10^{-4}$		
polymer	solvent	M:I	found[a]	calcd[b]	PDI
10a	CH_2Cl_2	40:1	1.34	1.00	1.30
10b	CH_2Cl_2	20:1	0.62	0.53	1.25
10b	CH_2Cl_2	40:1	1.34	1.01	1.15
10b	CH_2Cl_2	80:1	2.41	1.99	1.25
10b	CH_2Cl_2	160:1	4.53	3.93	1.38
10c	toluene	10:1	1.05	0.28	1.31
10c	toluene	20:1	2.03	0.52	1.19
10c	toluene	40:1	3.02	1.01	1.23
10c	toluene	60:1	4.23	1.49	1.20
10d	CH_2Cl_2	10:1	0.41	0.27	1.09
10d	CH_2Cl_2	20:1	0.83	0.52	1.20
10d	CH_2Cl_2	40:1	1.59	1.00	1.13

[a] Obtained by GPC vs polystyrene standards. [b] Calculated from the initial ratio of monomer to amino phosphoranimine initiator at 100% conversion.

Synthesis of a Mixed Telechelic Polyphosphazene. The control possible over the initiation and termination process for the living polymerization of **1** suggested the possible preparation of mixed telechelic polymers. The existence of two different functional groups on the ends of a polymer chain is an important attribute for synthesizing compounds of this nature. The different end groups can be used to produce A−B, A−B−A, or A−B−C type block copolymers either through the polymerization of monomers that undergo unrelated reaction mechanisms or through linking reactions with other telechelic polymers.[19]

Thus, the synthesis of a mixed telechelic polymer that contains the *p*-bromoanilino and allylamino end groups was undertaken (Scheme 5). The cationic initiator (**8d**) was first generated in a 1:2 molar reaction between the allylamino phosphoranimine (**5d**) and PCl_5 in CH_2Cl_2. Following complete formation of the initiator, 50 equiv of **1** was added to the reaction mixture to produce **9d**.

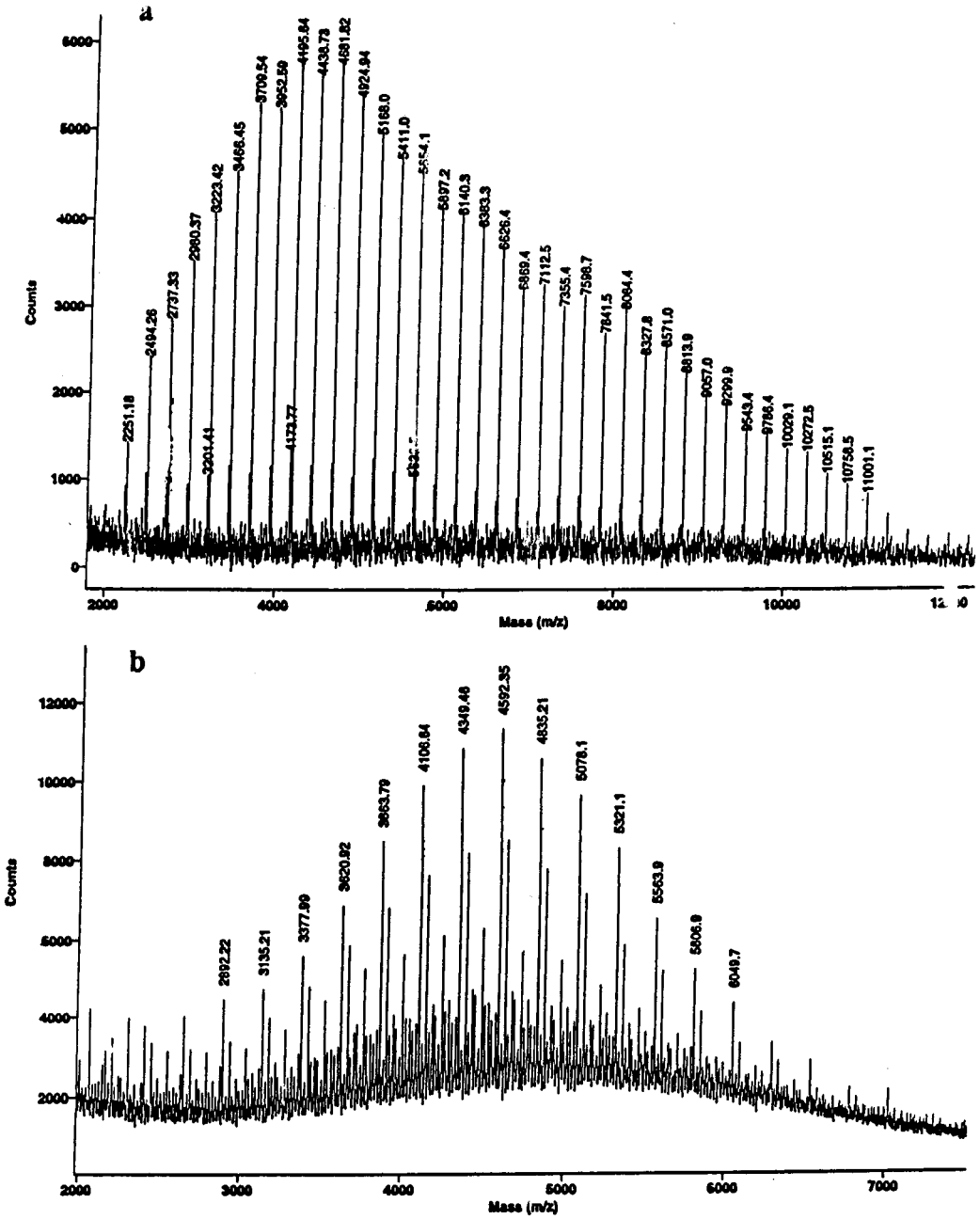


Figure 3. Comparative MALDI mass spectra for (a) $-[(CF_3CH_2O)_2P{=}N]_n-$ and (b) $[H_2C{=}CHCH_2N(H)]_2-[(CF_3CH_2O)_2P{=}N]_n-$.

Addition of the *p*-bromoanilino end cap (**5b**) resulted in the formation of a mixed telechelic poly(dichlorophosphazene) species (**11**) which was rendered hydrolytically stable by reaction with sodium trifluoroethoxide. The ^{1}H NMR spectrum obtained for polymer **12** indicated the presence of the bromoanilino resonances at 7.4−7.1 ppm while those of the allylamine end group appeared as multiplets at 5.4, 5.1, 4.7, and 3.6 ppm (Figure 4). In addition, the large multiplet present at 4.6−4.2 ppm is due to the trifluoroethoxy protons of the $[(CF_3CH_2O)_2P{=}N]_n$ repeat units along the polymer chain. GPC analysis of this material indicated a molecular weight versus polystyrene standards of 2.21×10^4 with a polydispersity index of 1.09.

Summary

The production of the first mono-, di-, and mixed-telechelic polyphosphazenes synthesized from various amino phosphoranimines and an ambient temperature polymerization process have been demonstrated. Both the efficiency and flexibility of this approach have been demonstrated by the ease of control of both the length of the polymer backbone and the nature of its end groups. In all instances, the polymers had narrow polydispersities and controlled molecular weights. These types of telechelic materials are important because of their potential use as macromonomers in the synthesis of block copolymers. Investigations involving the preparation of phosphazene−organic and phosphazene−inorganic block copolymers are currently underway in our laboratory.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide, allylamine, *p*-bromoaniline, *p*-toluidine, aniline, and 4-aminostyrene were obtained from Aldrich and were used without further purification. Phosphorus pentachloride (Aldrich) was purified by sublimation under vacuum prior to use. 1,1,1-Trifluoroethanol

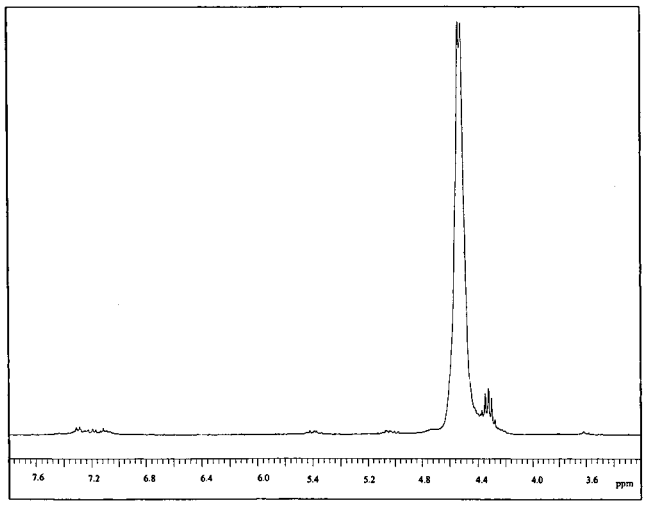
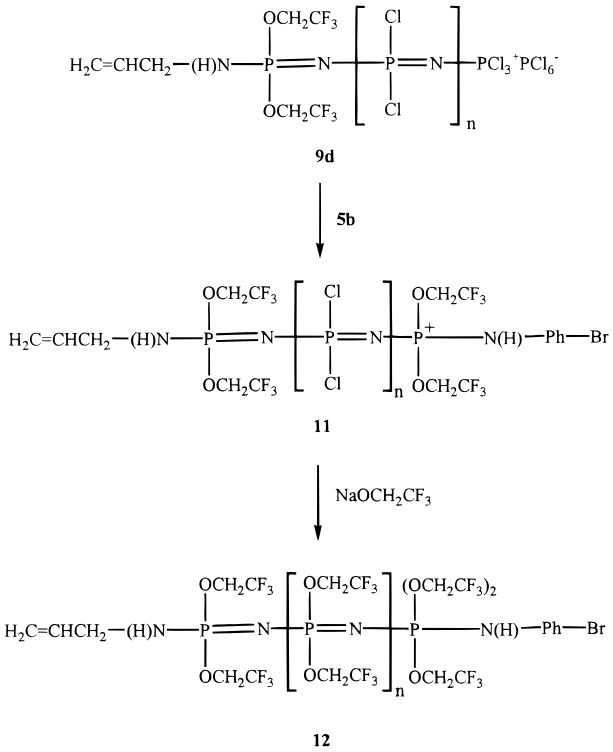


Figure 4. ^{1}H NMR (360 MHz) evidence for the preparation of a mixed telechelic polyphosphazene (**12**).

Scheme 5



was dried over CaH_2 and distilled before use. $Cl_3P{=}NSiMe_3$ and $Br(CF_3CH_2O)_2P{=}NSiMe_3$ were synthesized and purified by literature procedures.[9,30] Tetrahydrofuran, toluene, and hexane (Aldrich) were distilled into the reaction flask from sodium benzophenone ketyl under 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 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. ^{1}H, ^{13}C, and ^{31}P spectra were recorded on a Bruker WM-360 NMR spectrometer operated at 360, 146, and 90.27 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to solvent signals while ^{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 mm and AM gel 10 mm 10^4 Å column, and calibrated versus polystyrene standards (Polysciences). The samples were eluted at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). MALDI mass spectra were collected using a Voyager DESTR MALDI-TOF spectrometer.

Synthesis of Amino Phosphoranimines 5a−e. A mixture of $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**3**) (5.0 g, 12.59 mmol) and NEt_3 (1.27 g, 12.59 mmol) in THF (200 mL) was cooled to −78 °C in a dry ice/acetone bath. To this solution was added 12.59 mmol of the desired primary amine (**4a−e**) in 50 mL of THF over a period of 20 min. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. All volatiles were removed in vacuo, and the salts were washed with hexanes. After removal of the salts by filtration, the volatiles were removed under reduced pressure to leave the amino phosphoranimines (**5a−e**) as oils. These were isolated by distillation under high vacuum to yield the pure amino phosphoranimines.

For **5a:** Distillation under high vacuum (67−72 °C, 0.01 mmHg) gave 4.06 g (73%) of **5a**. ^{1}H NMR ($CDCl_3$): δ = 7.27 (d, J = 8.47 Hz, 2H, ArH), 7.50 (t, J = 7.13 Hz, 3H, ArH), 5.2 (br s, 1H, NH), 4.53−4.44 (m, 4H, OCH_2CF_3), 0.04 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ = −8.66 (s). ^{13}C NMR ($CDCl_3$): δ = 138.34 (1C, quaternary ArC), 128.41 (1C, ArC), 122.35 (q of d, J = 277.10, 5.75 Hz, 2C, $OCH_2\mathit{CF_3}$), 121.58, 117.60, 117,-51, 114.58 (4C, ArC), 61.53 (q of d, J = 37.41, 1.92 Hz, 2C, $O\mathit{CH_2}CF_3$), 1.69 (d, J = 1.78 Hz, 3C, $Si(CH_3)_3$). MS (CI): m/z = 409 (MH^+, 96%), 94 (PhNH, 100%)), in good agreement with isotopic abundance calculations.

For **5b:** Distillation under high vacuum (95 °C, 0.02 mmHg) gave 4.83 g (79%) of **5b**. ^{1}H NMR ($CDCl_3$): δ = 7.30 (d, J = 8.49 Hz, 2H, ArH), 6.78 (d, J = 8.86 Hz, 2H, ArH), 4.80 (br s, 1H, NH), 4.28−4.03 (m, 4H, OCH_2CF_3), 0.00 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ = −10.71 (s). ^{13}C NMR ($CDCl_3$): δ = 138.13 (1C, quaternary ArC), 132.27, 132.20 (2C, ArC), 122.84 (q of d, J = 277.45, 10.87 Hz, 2C, $OCH_2\mathit{CF_3}$), 119.77, 119.68 (2C, ArC), 114.90 (1C, quaternary ArC), 62.46 (q of d, J = 37.36, 3.81 Hz, 1C, $O\mathit{CH_2}CF_3$), 2.73 (d, J = 3.71 Hz, 3C, $Si(CH_3)_3$). MS (FAB+): m/z = 487 (MH^+, 100%), 472 ($M^+ - CH_3$, 76%), 316 (M^+ − NHPhBr, 22%), in good agreement with isotopic abundance calculations.

For **5c:** Distillation under high vacuum (109 °C, 1.4 mmHg) gave 4.52 g (85%) of **5c**. ^{1}H NMR ($CDCl_3$): δ = 7.08 (d, J = 8.22 Hz, 2H, ArH), 6.87 (d, J = 8.32 Hz, 2H, ArH), 4.82 (br s, 1H, NH), 4.34−4.14 (m, 4H, OCH_2CF_3), 2.30 (s, 3H, CH_3), 0.08 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ = −9.12 (s). ^{13}C NMR ($CDCl_3$): δ = 136.30, 132.03 (2C, quaternary ArC), 129.84, 118.37, 118.29 (4C, ArC), 124.49 (q of d, J = 277.53, 11.35 Hz, 2C, $OCH_2\mathit{CF_3}$), 62.39 (q of d, J = 37.39, 3.83 Hz, 1C, $O\mathit{CH_2}$-CF_3), 20.36 (s, $ArCH_3$), 2.74 (d, J = 3.60 Hz, 3C, $Si(CH_3)_3$). MS (+FAB): m/z = 422 (MH^+, 98.7%), 407 ($M^+ - CH_3$, 100%), in good agreement with isotopic abundance calculations.

For **5d:** Distillation under high vacuum (29 °C, 0.10 mmHg) gave 3.28 g (70%) of **5d**. ^{1}H NMR ($CDCl_3$): δ = 5.87 (m, 1H, $CH_2\mathit{CH}CH_2$), 5.14 (q, J = 6.38 Hz, 2H, $\mathit{CH_2}CHCH_2$), 3.52 (quin, J = 2.43 Hz, $CH_2CH\mathit{CH_2}$), 4.18 (quin, J = 3.65 Hz, $O\mathit{CH_2}CF_3$), 1.17 (t, J = 3.21 Hz, NH), 0.04 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ = −1.13 (s). ^{13}C NMR ($CDCl_3$): δ = 135.88 (d, J = 6.52 Hz, 1C, $CH_2\mathit{CH}CH_2$), 123.15 (q of d, J = 277.37, 10.96 Hz, 1C, $OCH_2\mathit{CF_3}$), 115.82 (1C, $\mathit{CH_2}CHCH_2$), 62.32 (q of d, J = 36.98, 4.23 Hz, $O\mathit{CH_2}CF_3$), 44.94 (1C, $CH_2CH\mathit{CH_2}$), 3.02 (d, J = 3.53 Hz, 3C, $Si(CH_3)_3$). MS (CI): m/z = 372 (MH^+, 64%), 356 ($M^+ - CH_3$, 10%) in good agreement with isotopic abundance calculations.

For **5e:** Distillation under high vacuum (65 °C, 0.01 mmHg) gave 4.26 g (78%) of **5e**. ^{1}H NMR ($CDCl_3$): δ = 7.08 (d, J = 4.20 Hz, 2H, ArH), 6.82 (d, J = 4.20 Hz, 2H, ArH), 6.50 (dd, J = 17.41, 3.30 Hz, 1H, $CH_2\mathit{CH}Ph$), 5.50, 5.02 (2d, J = 8.79, 5.42 Hz, 2H, $\mathit{CH_2}CHPh$), 4.22−4.06 (m, 4H, $O\mathit{CH_2}CF_3$), 1.07 (t, J = 3.60 Hz, 1H, NH), 0.18 (s, 9H, $Si(CH_3)_3$). ^{31}P NMR ($CDCl_3$): δ = −9.41. ^{13}C NMR ($CDCl_3$): δ = 137.88 (1C, quaternary ArC), 135.35 (1C, $CH_2\mathit{CH}Ph$), 131.32 (1C, quaternary ArC),

126.07 (2C, Ph), 121.99 (q of d, J = 277.00, 5.61 Hz, 1C, OCH2*CF*$_3$), 117.41, 117.33 (2C, Ph), 111.34 (1C, *CH*$_2$Ph), 61.65 (q of d, J = 37.13, 1.85 Hz, O*CH*$_2$CF$_3$), 1.89 (3C, d, J = 1.74 Hz, Si(CH$_3$)$_3$). MS (+FAB): m/z = 435 (MH$^+$, 100%), 419 (M$^+$ − CH$_3$, 85%) in good agreement with isotopic abundance calculations.

Preparation of Ditelechelic Polyphosphazenes 7a−e. A solution of 10 mg (0.048 mmol) of PCl_5 in 10 mL of CH_2Cl_2 or toluene was placed in a flask and was stirred for 1 h. A solution of **2** in 2 mL of CH_2Cl_2 was then added to the flask. The reaction mixture was monitored by ^{31}P spectroscopy until complete conversion of **1** to polymer had occurred. A slight excess of the desired amino phosphoranimine (**5a**−**e**) (based on the ratio of PCl_5:**1** used in the reaction) was then added, and the solution was stirred for 8 h. All volatiles were removed under reduced pressure, and the end-capped poly(dichlorophosphazene) (**6a**−**e**) was dissolved in 10 mL of THF. To this was added a 2-fold excess, per chlorine atom, of 1.5 M sodium trifluoroethoxide in THF, and the reaction mixture was stirred for 24 h at 25 °C. The derivatized polymer (**7a**−**e**) was then recovered via precipitation into deionized water (3×) and hexane (2×) or dialysis.

For **7a:** ^{1}H NMR (CD_3COCD_3): δ = 7.31−7.12 (m, 5H, ArH), 4.68 (d, J = 7.48 Hz, OCH$_2$CF$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.25 (s, [(CF$_3$CH$_2$O)$_2$P=N]$_n$), −1.61 (d, J = 65.07 Hz, PhNH-(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR not observed.

For **7b**: ^{1}H NMR (CD_3COCD_3): δ = 7.45−7.10 (m, 8H, ArH), 4.68−4.44 (m, O*CH*$_2$CF$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.31 (s, [(CF$_3$CH$_2$O)$_2$P=N]$_n$), −1.60 (d, J = 65.23 Hz, Br−PhNH-(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR (CD_3COCD_3): δ = 133.50, 132.62 (4C, quaternary ArC), 124.35 (q, J = 276.18 Hz, OCH$_2$*CF*$_3$), 123.93, 123.82 (8C, ArC), 64.54 (q, J = 37.76, O*CH*$_2$CF$_3$).

For **7c:** ^{1}H NMR (CD_3COCD_3): δ = 6.96 (d, J = 8.01 Hz, 4H, ArH), 6.84 (d, J = 7.98 Hz, 4H, ArH), 4.56−4.25 (m, O*CH*$_2$-CF$_3$), 2.15 (s, 6H, ArCH$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.28 (s, [(CF$_3$CH$_2$O)$_2$P=N]$_n$), −1.60 (d, J = 68.26 Hz, H$_3$CPh(HN)-(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR (CD_3COCD_3): δ = 130.99, 130.78 (4C, quaternary ArC), 124.00 (q, J = 276.70 Hz, OCH$_2$CF$_3$), 131.00 (s, 8C, ArC), 64.20 (q, J = 37.67, OCH$_2$CF$_3$), 20.96 (s, 2C, CH$_3$).

For **7d:** ^{1}H NMR (CD_3COCD_3): δ = 5.87 (m, 1H, CH$_2$*CH*CH$_2$), 5.14 (q, J = 6.38 Hz, 2H, *CH*$_2$CHCH$_2$), 3.52 (quin, J = 2.43 Hz, CH$_2$CH*CH*$_2$), 4.18 (m, O*CH*$_2$CF$_3$), 0.04 (s, 9H, Si(CH$_3$)$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.29 (s, [(CF$_3$CH$_2$O)$_2$P=N]$_n$), −1.85 (d, J = 67.09 Hz, CH$_2$CHCH$_2$(HN)(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR ($CDCl_3$): δ = 137.94 (1C, CH$_2$*CH*CH$_2$), 124.25 (q, J = 208.12, 1C, OCH$_2$*CF*$_3$), 114.72 (1C, *CH*$_2$CHCH$_2$), 63.25 (q, J = 33.25, O*CH*$_2$CF$_3$), 44.15 (1C, CH$_2$CH*CH*$_2$).

For **7e:** ^{1}H NMR (CD_3COCD_3): δ = 7.03 (b, 4H, ArH), 6.61 (b, 1H, CH$_2$*CH*Ph), 5.62, 5.09 (2d, J = 62.02 Hz, 2H, *CH*$_2$-CHPh), 4.55 (d, J = 7.56 Hz, 4H, O*CH*$_2$CF$_3$). ^{31}P NMR (CD_3-$COCD_3$): δ = −6.25 (s, [(CF$_3$CH$_2$O)$_2$P=N]$_n$), −1.85 (d, J = 67.07 Hz, CH$_2$=CHPhNH(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR (THF): δ = 139.33 (1C, quaternary ArC), 136.59 (1C, CH$_2$*CH*Ph), 132.33 (1C, quaternary ArC), 127.59 (2C, Ph), 123.98 (q, J = 276.22 Hz, 1C, OCH2*CF3*), 119.39 (2C, Ph), 111.34 (1C, *CH*$_2$-Ph), 64.00 (q, J = 37.13 Hz, O*CH*$_2$CF$_3$).

General Procedure for the Preparation of the Cationic Short Chain Initiators R−NH(CF$_3$CH$_2$O)$_2$P=NPCl$_3$]$^+$ [PCl$_6$]$^-$ (8a−d). To a stirred solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (toluene, **7c**) (200 mL) at −78 °C was added 0.25 mmol of the amino phosphoranimine (**5a**−**d**) quickly via syringe. The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature. ^{31}P NMR spectroscopy of the reaction mixture indicated the presence of the desired products as evidenced by two doublets for the terminal PCl_3^+ and the (CF$_3$CH$_2$O)$_2$P=N phosphorus atoms. The initiator solution was then used for the polymerization of **1** in the production of monotelechelic polyphosphazenes **10a**−**d**.

For **8a**: ^{31}P NMR (D_2O): δ = 10.39 (d, J = 49.39 Hz, (CF$_3$-CH$_2$O)$_2$P=N), 2.28 (d, J = 50.67 Hz, Cl$_3$P=N).

For **8b**: ^{31}P NMR (D_2O): δ = 11.06 (d, J = 48.04 Hz, (CF$_3$-CH$_2$O)$_2$P=N), 2.27 (d, J = 49.70 Hz, Cl$_3$P=N).

For **8c**: ^{31}P NMR (D_2O): δ = 10.14 (d, J = 52.67 Hz, (CF$_3$-CH$_2$O)$_2$P=N), 2.26 (d, J = 52.77 Hz, Cl$_3$P=N).

For **8d**: ^{31}P NMR (D_2O): δ = 4.22 (d, J = 52.61 Hz, (CF$_3$-CH$_2$O)$_2$P=N), −4.06 (d, J = 49.10 Hz, Cl$_3$P=N).

Polymerization of Cl$_3$P=NSiMe$_3$ (1) by R−NH-[(CF$_3$CH$_2$O)$_2$P=NPCl$_3$]$^+$ [PCl$_6$]$^-$ (8a−d) in Solution. To a stirred solution of the initiator (**8a**−**d**) in CH_2Cl_2 (toluene, **7c**) was added **1**. After a given amount of time (2−24 h, dependent on the monomer-to-initiator ratio), all the initial monomer (**1**) had reacted, as evidenced by the disappearance of the ^{31}P NMR resonance for **1** at −54 ppm and the presence of a new resonance at −17.6 ppm for [Cl$_2$P=N]$_n$. In general, the NMR spectra contained the following identical peaks. For R−NH-[(CF$_3$CH$_2$O)$_2$P=N−[Cl$_2$P=N]$_n$−PCl$_3$]$^+$[PCl$_6$]$^-$ **(9a**−**d)**: ^{31}P NMR (D_2O): δ = 8.2 (d, 1P, J = 29 Hz, −PCl$_3^+$), −14.5, −15.5 (t, 2P, J = 40 Hz, −*Cl*$_2$*P* = N−*Cl*$_2$*P*=N−[Cl$_2$P=N]$_n$), −17.6 ppm (br s, [N=PCl$_2$]$_n$). Following complete formation of the polymer, all volatile species were removed at reduced pressure. The residue was then dissolved in 10 mL of THF and treated with a 2-fold excess per chlorine atom of 1.5 M sodium trifluoroethoxide in THF. The mixture was stirred at 25 °C for 24 h to produce the corresponding macromolecule R−NH-[(CF$_3$CH$_2$O)$_2$P=N]$_n$ (**10a**−**d**). These polymers were isolated via precipitation into deionized water (3×) and hexane (2×).

For **10a**: ^{1}H NMR (CD_3COCD_3): δ = 7.31 (b, 5H, ArH), 4.68 (d, J = 7.48 Hz, OCH$_2$CF$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.25 (s, [(OCH$_2$CF$_3$)$_2$P=N]$_n$), −1.61 (d, J = 65.07 Hz, PhNH(CF$_3$-CH$_2$O)$_2$P=N), 2.56 (d, J = 65.07 Hz, N−P(OCH$_2$CF$_3$)$_4$). ^{13}C NMR not observed.

For **10b**: ^{1}H NMR (CD_3COCD_3): δ = 7.78−7.02 (m, 4H, ArH), 4.72−4.34 (m, O*CH*$_2$CF$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.29 (s, [(OCH$_2$CF$_3$)$_2$P=N]$_n$), −1.81 (d, J = 67.76 Hz, R(HN)-(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR (CD_3COCD_3): δ = 134.81, 132.63 (2C, quaternary ArC), 124.34 (q, J = 276.65 Hz, OCH$_2$CF$_3$), 118.62, 117.37 (4C, ArC), 64.33 (q, J = 37.67, OCH$_2$CF$_3$).

For **10c**: ^{1}H NMR (CD_3COCD_3): δ = 7.03 (d, J = 8.46 Hz, 2H, ArH), 6.94 (d, J = 8.30 Hz, 2H, ArH), 4.55−4.30 (m, O*CH*$_2$-CF$_3$), 2.16 (s, 3H, CH$_3$). ^{31}P NMR (CD_3COCD_3): δ = −6.26 (s, [(OCH$_2$CF$_3$)$_2$P=N]$_n$), −1.59 (d, J = 67.76 Hz, CH$_3$Ph−NH(CF$_3$-CH$_2$O)$_2$P=N). ^{13}C NMR (CD_3COCD_3): 134.59, 134.68 (2C, quaternary ArC), 131.02 (4C, ArC), 124.03 (q, J = 276.65 Hz, OCH$_2$CF$_3$), 64.23 (q, J = 37.63, OCH$_2$CF$_3$), 20.64 (ArCH$_3$).

For **10d**: ^{1}H NMR (CD_3COCD_3): δ = 5.81 (m, 1H, CH$_2$*CH*CH$_2$), 5.17, 4.98 (2m, 2H, J = 6.53, *CH*$_2$CHCH2), 4.37 (s, O*CH*$_2$CF$_3$), 3.52 (quin, J = 2.16 Hz, CH$_2$CH*CH*$_2$). ^{31}P NMR (CD_3COCD_3): δ = −6.29 (s, [(OCH$_2$CF$_3$)$_2$P=N]$_n$), −1.85 (d, J = 67.09 Hz, CH$_2$=CHCH$_2$(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR ($CDCl_3$): δ = 137.94 (1C, CH$_2$*CH*CH$_2$), 124.25 (q, J = 208.12, 1C, OCH$_2$*CF*$_3$), 114.72 (1C, *CH*$_2$CHCH$_2$), 63.25 (q, J = 33.25, O*CH*$_2$CF$_3$), 44.15 (1C, CH$_2$CH*CH*$_2$).

To control the molecular weight, the ratio of monomer (**1**) to initiator (**8a**−**d**) was varied by changing the amount of monomer while keeping all other amounts constant (see Table 2).

Synthesis of Mixed Telechelic Polyphosphazene 12. To a stirred solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 was added **5d** (0.093 g, 0.25 mmol) at −78 °C. The reaction mixture was stirred at −78 °C for 1 h and allowed to warm to room temperature. ^{31}P NMR spectroscopy of the reaction mixture indicated two doublets for **6d**. To this the initiator solution was added 50 equiv of **1** (2.8 g, 12.5 mmol), and the polymerization was monitored by ^{31}P NMR until complete conversion of **1** to polymer had occurred. A slight excess of **5b** (0.267 g, 0.55 mmol) was then introduced, and the reaction mixture was stirred for 8 h. All volatiles were removed under reduced pressure, and the polymer was dissolved in 10 mL of THF. To this was added a 2-fold excess, per chlorine atom, of 1.5 M sodium trifluoroethoxide in THF, and the reaction mixture was stirred for 24 h at 25 °C. Polymer **12** was then precipitated into deionized water (3×) and hexane (2×) to give an adhesive white solid.

For **12**: ^{1}H NMR (CD_3COCD_3): δ = 7.4−7.1 (m, 4H, Br−Ph), 4.79−4.81 (b, O*CH*$_2$CF$_3$), 5.85 (m, 1H, *CH*$_2$CHCH$_2$), 5.34 (quin, J = 6.47 Hz, CH$_2$CH*CH*$_2$). ^{31}P NMR (CD_3COCD_3): δ = −6.31 (s, [(OCH$_2$CF$_3$)$_2$P=N]$_n$), −1.59 (d, J = 33.87 Hz, CH$_2$=CHCH$_2$(CF$_3$CH$_2$O)$_2$P=N). ^{13}C NMR (THF): δ = 138.13 (1C, quaternary ArC), 132.27 (2C, ArC), 121.47 (q, J = 277.13

Hz, 2C, OCH_2CF_3), 119.77 (2C, ArC), 114.90 (1C, quaternary ArC), 61.66 (q, J = 37.76 Hz, 1C, OCH_2CF_3).

Acknowledgment. The authors thank the Federal Aviation Administration and the National Science Foundation Polymers Program for support of this work. J.M.N. and C.R.D. also thank the Natural Sciences and Engineering Research Council of Canada (NSERC) for Postdoctoral Research Fellowships.

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MA990318F