Telechelic Polyphosphazenes: Reaction of Living Poly(dichlorophosphazene) Chains with Alkoxy and Aryloxy Phosphoranimines

Harry R. Allcock,* Eric S. Powell, Andrew E. Maher, Robbyn L. Prange,† and Christine R. de Denus‡

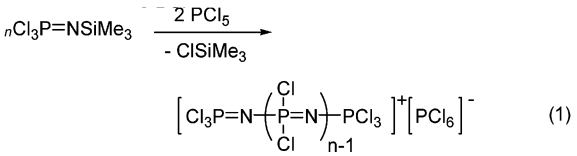
Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Received November 10, 2003; Revised Manuscript Received March 1, 2004

ABSTRACT: A modification of the method for synthesis of well-defined mono- and ditelechelic polyphosphazenes via the living, cationic polymerization of phosphoranimines has been developed. This process provides access to phosphazene block, comb, and graft copolymers that contain organic or organosilicon macromolecules. Several alkoxy and aryloxy phosphoranimines, $RO(CF_3CH_2O)_2P{=}NSiMe_3$ (R = Ph, MeOPh, $C_{10}H_7$, BOC−NH−CH_2CH_2, *t*-$BuMe_2SiO(CH_2)_5$, C_8H_{11}, and $CH_2{=}CH{-}C_6H_4$), were synthesized via the reaction between a bromophosphoranimine and the appropriate sodium alkoxide or aryl oxide. These species are potential initiators or terminators, useful for the synthesis of telechelic polyphosphazenes with etheric linkages rather than the amino linkages used previously. Ditelechelic polymers, $RO[(CF_3CH_2O)_2P{=}N]_n{-}P(OCH_2CF_3)_3OR$, were prepared by terminating living poly(dichlorophosphazene) chains, $[Cl_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$, with these alkoxy or aryloxy phosphoranimines. Alternatively, monotelechelic polyphosphazenes were produced through the termination of the polymer $[(CF_3CH_2O_2)_3P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$ with the appropriate alkoxy or aryloxy phosphoranimines. In all cases, hydrolytically stable telechelic polymers with controlled molecular weights and low polydispersities were obtained in good yield after macromolecular replacement of labile chlorine atoms with sodium trifluoroethoxide.

Introduction

The synthesis of hybrid macromolecules that combine polyphosphazenes with organic polymers is an essential component in the development of polymeric systems that contain the attributes of both types of systems.[1,27] One method that allows such hybrid systems to be produced utilizes the living, cationic polymerization of phosphoranimines, shown in its simplest form in reaction 1.[2,3] Poly(dichlorophosphazene) produced in this manner can be converted to a wide variety of poly(organophosphazenes) by macromolecular replacement of the chlorine atoms by organic or organometallic nucleophiles.



(1)

The utilization of this pathway for the production of hybrid organic−inorganic block, comb, or graft copolymers requires the use of specific phosphoranimine initiators and terminators.[4−10] These organophosphoranimines have a general formula of $X{-}P(R)(R'){=}NSiMe_3$, where R and R′ represent unreactive organic groups, and X can be either an organic linker that bears a functional group or a polymeric chain. If X is an organic polymer, then termination by or initiation from this species will directly give a hybrid organic−inorganic polymer. If X contains a functional group, such as a vinyl, allyl, or protected hydroxyl or amino group, then the resultant telechelic polyphosphazene may be subjected to further reactions to generate block copolymers using reactive end groups as linkages or graft copolymers by addition polymerization through unsaturated end groups.

Earlier work focused on initiating and terminating species in which a functional group was linked to the end of the polyphosphazene chain through amino units.[4] It was considered useful for future work to study etheric linkages as well as amine linkages. This would increase the number of functional groups available for the synthesis of telechelic polyphosphazenes and reduce the possibility that the linkages between the polymer backbone and the telechelic group could be cleaved in acidic media. Thus, here we describe the synthesis of several oxygen-linked phosphoranimine species and demonstrate their usefulness as terminators for the synthesis of mono- and ditelechelic polyphosphazenes via the living, cationic polymerization of phosphoranimines.

Results and Discussion

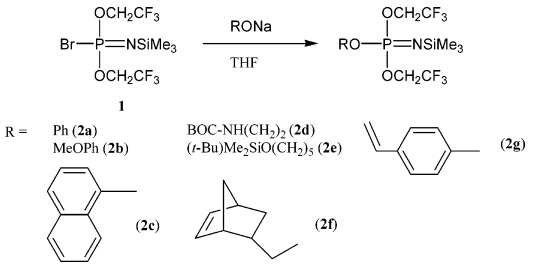
Synthesis of Functional Phosphoranimines $R{-}O{-}(CF_3CH_2O)_2P{=}NSiMe_3$ (2a−g). Phosphoranimines such as $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**1**) are known to undergo bromine replacement reactions with various metal alkoxides to produce $R{-}O(CF_3CH_2O)_2P{=}NSiMe_3$ species.[10,11] With this in mind, stoichiometric amounts of different sodium alkoxides and aryloxides, RONa, were allowed to react with **1** in THF at −78 °C to produce the corresponding alkoxy or aryloxy phosphoranimines, $R{-}O(CF_3CH_2O)_2P{=}NSiMe_3$ (R = Ph (**2a**), MeOPh (**2b**), $C_{10}H_7$ (**2c**), BOC−NH−CH_2CH_2 (**2d**), *t*-$BuMe_2SiO(CH_2)_5$

† Present address: The Dow Chemical Corporation, 2301 Brazosport Rd., B. 1608, Freeport, TX 77541.

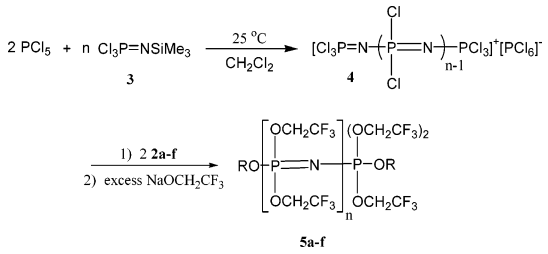
‡ Present address: Department of Chemistry, Hobart and William Smith Colleges, Geneva, NY 14456.

10.1021/ma030554x CCC: $27.50
Published on Web 04/22/2004

Scheme 1



Scheme 2



(**2e**), C_8H_{11} (**2f**), and $CH_2{=}CH{-}C_6H_4$ (**2g**)) (Scheme 1), in good yields. These phosphoranimines were used as terminators in subsequent phosphazene polymerization reactions. The objective of this was to utilize these phosphoranimines as alternatives to the aminophosphoranimines used in earlier work.

The functional groups present on these phosphoranimines enable them to be used either in organic transformations or directly in polymerization reactions. For instance, amino-terminated polyphosphazenes should be accessible through nitration and subsequent reduction of a phenoxy end group or by deprotection of BOC-terminated species. In addition, the 1-naphthoxy end group opens the possibility of Scholl-type polymerizations, while the 5-norbornene-2-methoxy end group is suitable for ring-opening metathesis polymerization (ROMP) reactions. It has already been demonstrated that 4-vinylanilino-substituted phosphoranimines (−NH-linked species) can be used to synthesize polyphosphazenes with a reactive styryl end group, which allows their subsequent incorporation into graft copolymers.[12] The 4-vinylphenoxy derivative discussed here (−O-linked species) should undergo the same types of reactions. Finally, deprotection of a TBDMS end group should allow the preparation of a hydroxyl-terminated polyphosphazene. All of these materials are important for future investigations into block, comb, and graft copolymer formation.

Synthesis of Ditelechelic Polyphosphazenes (5a−f). A recent report from our laboratory has shown that the addition of 2 equiv of a phosphoranimine with an amino-linked functional group to a living chain of poly(dichlorophosphazene) (**4**) allows the controlled introduction of *two* functional terminal units onto the polymer chain.[4] This arises because the cationic terminus of a living cationic polymerization can be delocalized to both ends of the macromolecule. Thus, for comparison, ditelechelic polymers **5a−f** were prepared as outlined in Scheme 2, using alkoxy or aryloxy phosphoranimines to terminate living poly(dichlorophosphazene) at both ends. For these materials, the length of the poly(dichlorophosphazene) chain was controlled by the molar ratio of $Cl_3P{=}NSiMe_3$ to PCl_5 in the initial step of the reaction, and the terminator was then introduced in the appropriate molar ratio. In all instances, the resultant polymers were isolated in good yield after replacement of the chlorine atoms by sodium trifluoroethoxide. The final polymers ranged in physical properties from viscous liquids to solids, depending on their molecular weight.

Table 1. Molecular Weight Data for Ditelechelic Polymers 5a−f

		$M_n \times 10^{-4}$		
polymer	M:I	calculated[a]	found[b]	PDI
5a	10:1	0.55	0.99	1.26
5a	20:1	1.04	2.10	1.10
5a	40:1	2.01	2.79	1.14
5a	60:1	2.98	3.29	1.17
5b	10:1	0.56	1.05	1.18
5b	20:1	1.05	1.67	1.24
5b	40:1	2.02	5.67	1.05
5b	60:1	2.99	5.10	1.06
5c	10:1	0.56	1.68	1.13
5c	20:1	1.05	2.03	1.18
5c	40:1	2.02	4.82	1.08
5c	60:1	2.99	4.62	1.07
5d	10:1	0.57	0.92	1.08
5d	20:1	1.05	1.59	1.14
5d	40:1	2.02	3.36	1.11
5d	60:1	3.00	4.91	1.16
5e	10:1	0.58	0.90	1.08
5e	20:1	1.06	1.75	1.17
5e	40:1	2.04	3.07	1.11
5e	60:1	3.01	4.15	1.19
5f	10:1	0.56	1.03	1.18
5f	20:1	1.05	1.27	1.24
5f	40:1	2.02	4.73	1.07
5f	60:1	2.99	5.47	1.47

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

The polymers were characterized using multinuclear NMR spectroscopy and gel permeation chromatography (GPC). ^1H, ^{13}C, and ^{31}P NMR spectroscopy were utilized to detect the presence of the new end groups introduced via the alkoxy and aryloxy phosphoranimines. The molecular weights of these polymers, as determined by gel permeation chromatography against polystyrene standards, ranged from 0.90×10^4 to 8.38×10^4 (Table 1). In all cases, the polymers were obtained with low polydispersities. The low polydispersities are attributed to the living nature of the polymerization process, while the discrepancy between the calculated and GPC molecular weights is probably due to an overestimation of molecular weight by GPC.[13] It was also found that the molecular weights of the polymers increased as the monomer-to-initiator ratio was increased, as illustrated in Table 1.

Synthesis of Monotelechelic Polyphosphazenes (9a−g). Monotelechelic materials are important for the production of diblock copolymers with a high degree of architectural control. Monotelechelic materials are also useful as preformed building blocks in graft or comb copolymer syntheses and would eliminate possible crosslinking that might arise from bifunctional species. Thus, we investigated the preparation of such polymers by the process outlined in Scheme 3.

Two molar equivalents of PCl_5 was allowed to react with the initiating phosphoranimine $(CF_3CH_2O)_3P{=}NSiMe_3$ at 25 °C in CH_2Cl_2 to generate the initiating species $[(CF_3CH_2O)_3P{=}N{-}PCl_3]^+[PCl_6]^-$ (**7**). This ensured that only one end of the living poly(dichlorophosphazene) chain remained reactive. The formation of this initiator was confirmed in situ by the presence of two doublets in the ^{31}P NMR spectrum for the $N{-}PCl_3^+$ and

Scheme 3

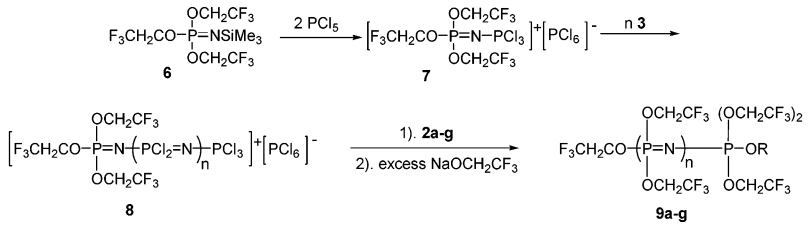


Table 2. Molecular Weight Data for Monotelechelic Polymers 9a−g

		$M_n \times 10^{-4}$		
polymer	M:I	calculated[a]	found[b]	PDI
9a	10:1	0.52	1.15	1.10
9a	20:1	1.01	1.59	1.22
9b	5:1	0.26	0.49	1.10
9b	10:1	0.53	1.29	1.08
9c	20:1	1.01	1.55	1.19
9d	20:1	1.01	1.70	1.10
9d	40:1	1.98	2.64	1.12
9d	60:1	2.96	4.14	1.14
9e	10:1	0.53	0.94	1.28
9e	20:1	1.02	1.46	1.31
9e	40:1	1.99	2.52	1.08
9e	60:1	2.96	3.73	1.04
9f	10:1	0.53	1.25	1.19
9f	12:1	0.65	1.46	1.14
9f	20:1	1.02	1.87	1.17
9g	20:1	1.02	1.67	1.13

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

$(CF_3CH_2O)_3P{=}N$ units. Subsequent addition of given amounts of $Cl_3P{=}NSiMe_3$ (**3**) to the reaction mixture containing **7** resulted in the formation of living poly(dichlorophosphazene) (**8**) with controlled chain lengths. The progress of each reaction was monitored by ^{31}P NMR spectroscopy, and it was found that all polymerizations were complete within 24 h at 25 °C. Monotelechelic materials were then obtained by termination of these living poly(dichlorophosphazene) chains, by the addition of 1.1 equiv of a functional phosphoranimine terminator (**2a**−**g**) to the reaction mixture that contained **8**. Macromolecular replacement of the chlorine atoms with sodium trifluoroethoxide or sodium phenoxide then yielded the hydrolytically stable derivative polymers **9a**−**g**. All polymers were characterized by the spectroscopic and analytical methods mentioned previously. The molecular weights, obtained from GPC vs polystyrene standards, ranged from 0.94×10^4 to 4.14×10^4 (Table 2). Although phosphoranimines **2a**−**g** performed well as terminators for the living, cationic polymerization of $Cl_3P{=}NSiMe_3$, attempts to *initiate* polymerization from them gave inconsistent chain lengths, decreased molecular weight control, and broad polydispersities. Thus, monotelechelic polyphosphazenes could not be obtained by the growth of a polyphosphazene from these phosphoranimines.

Characterization of Mono- and Ditelechelic Polyphosphazenes. The ^{31}P NMR spectra in Figures 1 and 2 illustrate the changes that occur during the synthesis of a monotelechelic polyphosphazene. Figure 1 shows a typical ^{31}P NMR spectrum for the initiating species **7**, with doublets at 22.78 and −9.91 ppm. Figure 2a shows the ^{31}P NMR spectra for polymer **8**, obtained after the phosphoranimine **3** has been polymerized from the initiating species **7**. The peaks in Figure 2a are assigned as follows: +8 ppm (d, terminal PCl_3^+), −12 ppm (d, $(CF_3CH_2O)_3P$), −14 ppm (t, $-PCl_2{=}N{-}PCl_3$), −15 ppm (t, $-Cl_2P{=}N{-}Cl_2P{=}N{-}PCl_3$), and −17 ppm (br s, $[Cl_2P{=}N]_n$). The living poly(dichlorophosphazene) chain was terminated by the addition of phosphoranimine **2f**, as indicated by the disappearance of the resonance for the PCl_3^+ unit and the appearance of a new resonance for the 5-norbornene-2-methoxy-P at −7 ppm (Figure 2b).

MALDI mass spectrometry was carried out on representative samples of these new materials.[28] The MALDI spectra of a di- and monotelechelic polymer, **5e** and **9b**, are shown in Figure 3. Figure 3a (polymer **5e**) shows a series of signals that are representative of the

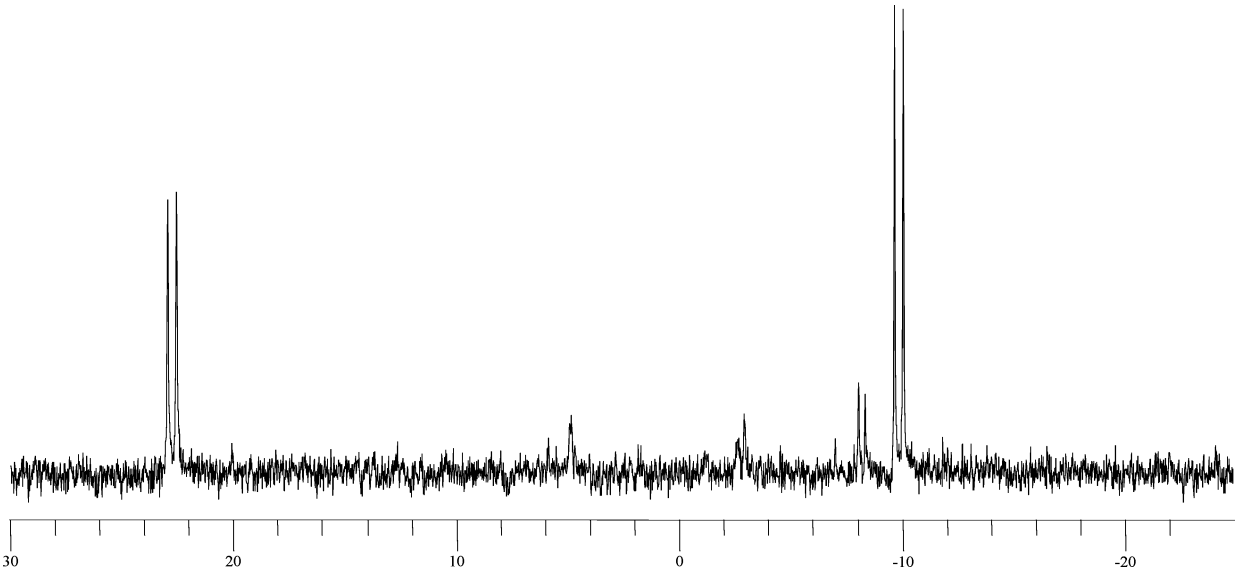


Figure 1. ^{31}P NMR spectrum of the initiating species $[(CF_3CH_2O)_3P{=}NPCl_3]^+[PCl_6]^-$ (**7**).

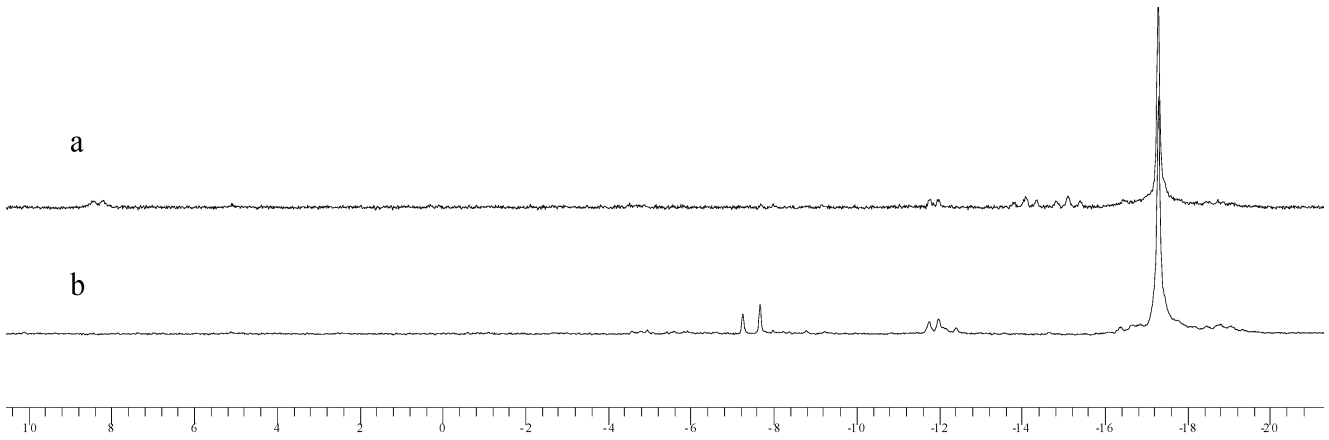


Figure 2. ^{31}P NMR spectrum of (a) a living poly(dichlorophosphazene) chain initiated from **7** and (b) a slight excess of alkoxy phosphoranimine **2f** added to quench the polymerization process.

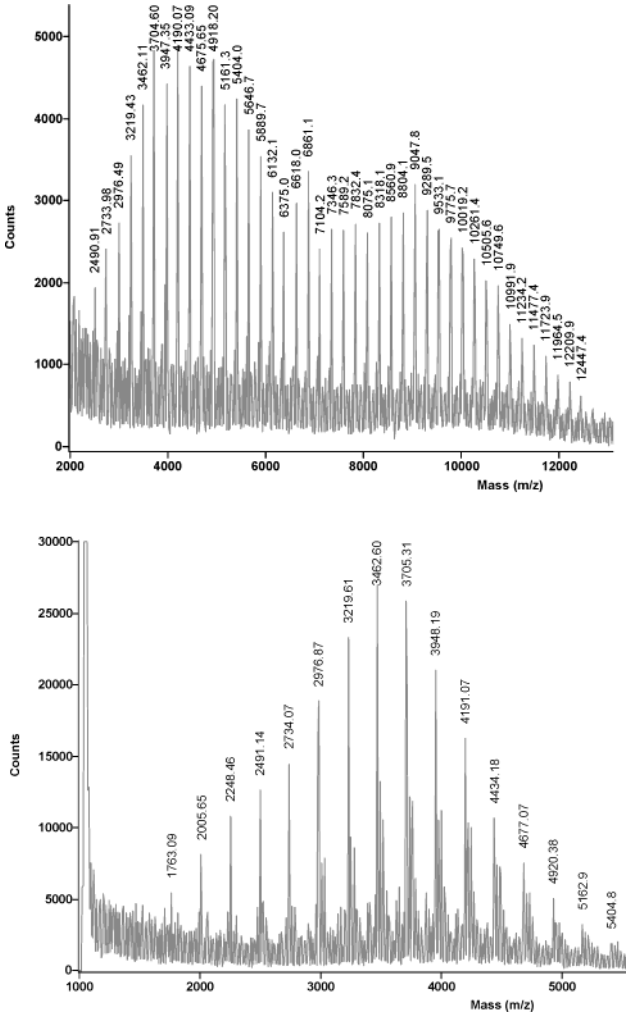
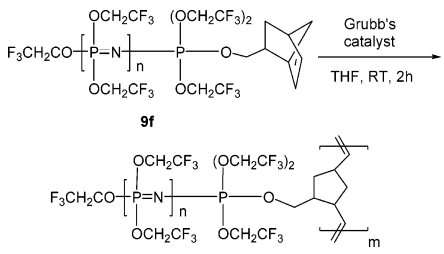


Figure 3. MALDI mass spectra of (a) ditelechelic polymer **5e** and (b) monotelechelic polymer **9b**.

average repeat unit $[(CF_3CH_2O)_2P{=}N]_{20}$ (mass 4860), the $P{-}(OCH_2CF_3)_3$ transition group (mass 328), the two end groups, *t*-$BuMe_2SiO(CH_2)_5{-}O$ (mass 434), and a sodium ion for a total mass of approximately 5645. Figure 3b (polymer **9b**) has a similar signal pattern with the average mass signal of approximately 3463 arising from the average repeat unit $[(CF_3CH_2O)_2P{=}N]_{12}$ (mass 2916), the $-P{-}(OCH_2CF_3)_3$ transition groups (mass 328), and the two end groups, $-OC_6H_4{-}O{-}CH_3$ and $CF_3CH_2O{-}$ (mass 223). The smaller secondary peaks

Scheme 4



that trail the major signals in Figure 3b are indicative of multiple sodium ion additions to the polymer backbone and do not support the existence of multiple chain structures. In both spectra the series of signals are representative of polymer chains with the repeating unit $[(CF_3CH_2O)_2P{=}N]_n$, where the distance between the peaks is calculated to be that of the repeating unit's mass, 243 g/mol. These findings support that the polymer chains are telechelic in nature, were synthesized without any structural changes to the backbone, and contain functional groups only at the terminus of the polymer chains.

Differential scanning calorimetry was used to examine the effect of the various telechelic end groups on the glass transition temperatures of the synthesized polymers. Ditelechelic polymers **5a**−**f** and monotelechelic polymers **9a**−**g** all showed a T_g of −66 °C, characteristic of poly[bis(trifluoroethoxy)phosphazene] homopolymer. This demonstrates that the presence of the functional end groups on the polymers in this study did not affect the T_g values. This allows for the synthesis of hybrid copolymers via telechelic polyphosphazenes without unwanted alteration of thermal properties of the phosphazene block.

Reactivity Investigations. Polymer **9f**, with various chain lengths, undergoes ROMP reactions with Grubbs' catalyst in THF (Scheme 4), in a manner similar to that described for other phosphazene-functionalized norbornenes. The synthesis and characterization of these types of polymers are reported elsewhere.[14,15] It has also been found that polymer **9g** copolymerizes with styrene and methyl methacrylate, in the same manner as the vinylanilino-terminated polyphosphazene previously reported, to yield a polystyrene- or poly(methyl methacrylate)-*graft*-polyphosphazene copolymer.[12,26] Polymers **9f** and **9g** demonstrate the reactivity and utility of telechelic polyphosphazenes. However, initial studies into the Scholl polymerization behavior of the ditelechelic

1-naphthoxy polymers (**5c**) have shown that these materials resist polymerization under the reaction conditions described in the literature.[16−18] Polymer **5e** has been deprotected to its free hydroxyl derivative. Both IR and ^{1}H NMR spectroscopy have confirmed that reagents for cleavage of the TBDMS group, such as tetrabutylammonium fluoride, boron trifluoride, HCl, pyridinium *p*-toluenesulfonate, and a Pd catalyst give the terminal hydroxyl unit in moderate yields.[19−24]

Conclusions

The preparation of mono- and ditelechelic polyphosphazenes using alkoxy or aryloxy phosphoranimines and an ambient temperature polymerization process have been carried out. These alkoxy and aryloxy derivatives are shown to work best as terminators for the cationic polymerization process rather than as initiators. The length of the polymer backbone and nature of its end groups were controlled to produce polymers with narrow polydispersities, predetermined molecular weights, and well-defined structures with functional groups only at the termini of the polymer chains. In addition, monotelechelic polymers **9f** and **9g** have been polymerized via their end groups using ROMP methods or under free radical conditions to yield graft copolymers. These examples illustrate that use of alkoxy or aryloxy phosphoranimines is a viable alternative to the use of amino-linked phosphoranimines and provides a more stable linkage for the synthesis of block and graft copolymers.

Experimental Section

Materials. Lithium bis(trimethylsilyl)amide, phenol, *p*-methoxyphenol, 5-(*tert*-butyldimethylsilyloxy)-1-pentanol, *N*-(*tert*-butoxycarbonyl)ethanolamine, 5-norbornene-2-methanol, and 95% sodium hydride were obtained from Aldrich and were used without further purification. Phosphorus pentachloride (Aldrich) was purified by sublimation under vacuum prior to use. 1-Naphthol was recrystallized from a deionized water/ethanol mixture before use. 2,2,2-Trifluoroethanol was dried over calcium hydride (CaH_2) and distilled before use. $Cl_3P{=}NSiMe_3$, $Br(CF_3CH_2O)_2P{=}NSiMe_3$, $(CF_3CH_2O)_3P{=}NSiMe_3$, and 4-vinylphenol were synthesized and purified by literature procedures.[11,25] Tetrahydrofuran (THF), toluene, and hexanes (Aldrich) were distilled into the reaction flask from sodium benzophenone ketyl under an atmosphere of dry argon. Dichloromethane (CH_2Cl_2) (Aldrich) was dried over $CaSO_4$ and distilled from CaH_2 into the reaction flask.

All glassware was dried overnight in an oven at 125 °C or flame-dried under vacuum before use. Reactions were carried out using standard Schlenk techniques or an inert atmosphere glovebox (Vacuum Atmospheres or MBraun) under an atmosphere of dry argon or nitrogen.

Equipment. ^{1}H, ^{13}C, and ^{31}P spectra were obtained using a Bruker AMX-360 NMR spectrometer, operated at 360 and 146 MHz. ^{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. All chemical shifts are reported in ppm. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and American Polymer Standards AM gel 10 mm and AM gel 10 mm 104 Å analytical columns and calibrated against 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).

Synthesis of Alkoxy and Aryloxy Phosphoranimines 2a−g. A solution of $Br(CF_3CH_2O)_2P{=}NSiMe_3$ (**1**) (5.0 g, 12.59 mmol) in THF (200 mL) was cooled to −78 °C in a dry ice/acetone bath. A quantitative amount of the desired sodium salt (prepared via reaction of the appropriate alcohol with sodium hydride in 50 mL of THF) was added to this solution over a period of 20 min. The reaction mixture was allowed to warm slowly to room temperature and was stirred overnight. ^{31}P NMR spectroscopy was used to verify complete conversion of **1** to the corresponding functional phosphoranimine. Salts were removed by filtration under an inert atmosphere, and all volatiles were removed under reduced pressure. The resultant oils were purified by distillation under high vacuum to yield the alkoxy/aryloxy phosphoranimines **2a**−**g** in good yields.

For **2a**: Distillation under reduced pressure (114 °C, 10 mmHg) gave a 72% yield. ^{1}H NMR ($CDCl_3$): δ = 7.34 (t, 2H), 7.13−7.21 (m, 3H), 4.30−4.39 (m, 4H), 0.00 (s, 9H). ^{31}P NMR ($CDCl_3$): δ = −16.55 (s). ^{13}C NMR ($CDCl_3$): δ = 150.69, 122.9, 129.72, 125.41, 120.54, 120.49, 63.72, 2.45. MS (CI): m/z = 409 (MH+, 100%), 397 (M−C_6H_5, 83%), in good agreement with isotopic abundance calculations.

For **2b**: Distillation under reduced pressure (70 °C, 20 mmHg) gave a 52% yield. ^{1}H NMR ($CDCl_3$): δ = 7.05 (d, 2H), 6.86 (d, 2H), 4.27−4.38 (m, 4H), 3.80 (s, 3H), 0.00 (s, 9H). ^{31}P NMR ($CDCl_3$): δ = −15.87 (s). ^{13}C NMR ($CDCl_3$): δ = 157.20, 144.28, 122.96, 121.47, 121.42, 114.67, 63.74, 55.48, 2.59. MS (FAB+): m/z = 440 (MH+, 77%), 424 (M−CH_3, 100%), in good agreement with isotopic abundance calculations.

For **2c**: Distillation under reduced pressure (115 °C, 10 mmHg) gave a 68% yield. ^{1}H NMR ($CDCl_3$): δ = 8.20 (d, 1H), 7.91 (d, 1H), 7.75 (d, 2H), 7.39−7.65 (m, 1H), 4.41−4.54 (m, 4H), 0.03 (s, 9H). ^{31}P NMR ($CDCl_3$): δ = −16.78 (s). ^{13}C NMR ($CDCl_3$): δ = 146.63, 146.54, 135.08, 128.06, 126.74, 126.49, 125.27, 121.63, 115.41, 115.37, 124.28−127.46, 63.76, 2.43. MS (CI): m/z = 459 (MH+, 89%), 332 (M−$C_{10}H_7$, 73%), in good agreement with isotopic abundance calculations.

For **2d**: Distillation under reduced pressure (93 °C, 10 mmHg) gave a 65% yield. ^{1}H NMR ($CDCl_3$): δ = 4.22 (m, 4H), 1.75 (t, 2H), 1.45 (s, 9H), 1.24 (t, 2H), 0.13 (d, 9H). ^{31}P NMR ($CDCl_3$): δ = −16.3. ^{13}C NMR ($CDCl_3$): δ = 124.6, 63.5, 65.5, 32.2, 30.1, 28.2, 2.1. MS (FAB+): m/z = 403 (MH+ −$SiMe_3$, 90%), 387 (MH+ −$SiMe_3$−Me, 63%) in good agreement with isotopic abundance calculations.

For **2e**: Distillation under reduced pressure (84 °C, 10 mmHg) gave a 64% yield. ^{1}H NMR ($CDCl_3$): δ = 4.17 (m, 4H), 3.56 (q, 4H), 1.48−1.54 (m, 4H), 1.34−1.36 (m, 2H), 0.84 (s, 9H), 0.02 (s, 6H), 0.00 (s, 9H). ^{31}P NMR ($CDCl_3$): δ = −8.91 (s). ^{13}C NMR ($CDCl_3$): δ = 121.65, 62.0, 64.1, 28.7, 45.2, 41.3, 30.8, 24.2, 1.4. MS: (FAB+) m/z = 533 (MH+, 25%), 518 (M+ −CH_3, 35%), 434 (M+ −CH_3−OCH_2CF_3, 21%) in good agreement with isotopic abundance calculations.

For **2f**: Distillation under reduced pressure (110 °C, 5 mmHg) gave a 77% yield. ^{1}H NMR ($CDCl_3$): δ = 6.16−6.19 (m, 1H), 6.10 (br s, 1H), 5.93−5.96 (m, 1H), 4.19−4.28 (m, 4H), 3.72−3.76 (m, 2H), 3.52−3.60 (m, 2H), 2.92, 2.83, 2.76 (3 br s, 4H), 2.37−2.45 (m, 1H), 1.75−1.86 (m, 2H), 1.44−1.49 (m, 1H), 1.23−1.30 (m, 1H), 1.02−1.16 (m 1H), 0.49−0.55 (m, 1H), 0.06 (br s, 9H). ^{31}P NMR ($CDCl_3$): δ = −8.18 (s). ^{13}C NMR ($CDCl_3$): δ = 138.33, 137.73, 136.92, 133.04, 124.24, 72.37, 71.72, 63.31−64.53, 49.89, 45.42, 44.40, 44.05, 42.98, 42.35, 40.27, 40.00, 29.69, 29.08, 3.16. MS (FAB+): m/z = 439 (MH+, 21%), 316 (M−$C_8H_{11}O$, 35%), in good agreement with isotopic abundance calculations.

For **2g**: Distillation under reduced pressure (95 °C, 10 mmHg) gave a 67% yield. ^{1}H NMR ($CDCl_3$): δ = 7.39 (d, 2H), 7.10 (d, 2H), 6.69 (m, 1H), 5.71 (d, 1H), 5.25 (d, 1H), 4.35 (m, 4H), 0.06 (d, 9H). ^{31}P NMR ($CDCl_3$): δ = −17.15 (s). ^{13}C NMR ($CDCl_3$): δ = 150.75, 143.29, 137.45, 122.54, 130.05, 125.42, 120.53, 61.25, 2.40. MS (CI): m/z = 436 (MH+, 65%), in good agreement with isotopic abundance calculations.

Typical Synthesis of Ditelechelic Polyphosphazenes 5a−f. Phosphorus pentachloride (100 mg, 0.48 mmol, 2 equiv) was dissolved in 10 mL of CH_2Cl_2 under an argon atmosphere for 1 h. Once the PCl_5 had dissolved completely, 540 mg (2.4 mmol, 10 equiv) of **3** was added. The reaction was monitored by ^{31}P NMR spectroscopy until complete conversion of **3** to polymer had occurred. To this solution was added 210 mg (5.0

mmol, 2.1 equiv) of compound **2a**, and the solution was stirred at 25 °C for 6−24 h. After confirmation of complete termination of polymerization by ^{31}P NMR spectroscopy (as determined by the disappearance of the resonance at +8 ppm), all volatiles were removed under reduced pressure, and the end-capped poly(dichlorophosphazene) was subsequently redissolved in 10 mL of THF. To this solution was added 3 mL of a 2.0 M solution of $NaOCH_2CF_3$ in THF. The resultant mixture was stirred for 24 h at room temperature, after which the complete replacement of all chlorine atoms was confirmed by ^{31}P NMR spectroscopy. The derivatized polymer **5a** was recovered and purified via precipitation from THF into deionized water (3×) and hexanes (2×).

For **5a**: ^{1}H NMR (acetone-d_6): $\delta = 7.40$ (t, 6H), 7.26 (d, 4H), 4.28−4.66 (m, OCH_2CF_3). ^{31}P NMR (acetone-d_6): $\delta = -6.48$ (s), −1.84 (d). ^{13}C NMR (acetone-d_6): 130.65, 121.68, 121.62, 124.02, 64.21.

For **5b**: ^{1}H NMR (acetone-d_6): $\delta = 7.06$ (d, 4H), 6.79 (d, 4H), 4.17−4.41 (m, OCH_2CF_3), 3.65 (s, 6H). ^{31}P NMR (acetone-d_6): $\delta = -6.29$ (s), −1.67 (d). ^{13}C NMR (acetone-d_6): 158.36, 145.34, 145.24, 124.07, 122.53, 115.47, 64.24, 55.82.

For **5c**: ^{1}H NMR (acetone-d_6): $\delta = 8.26-8.27$ (m, 2H), 7.94 (br s, 2H), 7.80 (d, 2H), 7.41−7.65 (m, 8H), 4.26−4.93 (m, OCH_2CF_3). ^{31}P NMR (acetone-d_6): $\delta = -6.32$ (s), −1.62 (d). ^{13}C NMR (acetone-d_6): 150.83, 135.88, 128.81, 128.62, 127.78, 127.45, 126.27, 124.03, 116.56, 64.18.

For **5d**: ^{1}H NMR ($CDCl_3$): $\delta = 4.36$ (m, OCH_2CF_3), 1.83 (t, 2H), 1.51 (s, 9H), 1.30 (t, 2H). ^{31}P NMR ($CDCl_3$): $\delta = -6.48$ (s), −16.1 (br s). ^{13}C NMR ($CDCl_3$): $\delta = 123.4$, 63.0, 64.2, 31.8, 39.7, 28.5, 2.8.

For **5e**: ^{1}H NMR ($CDCl_3$): $\delta = 4.23$ (quin, 4H), 3.59 (q, 4H), 1.50−1.56 (m, 4H), 1.38−1.44 (m, 2H), 0.87 (s, 9H), 0.03 (s, 6H). ^{31}P NMR ($CDCl_3$): $\delta = -9.20$ (s). ^{13}C NMR ($CDCl_3$): $\delta =$ 121.65, 61.0, 61.3, 26.7, 44.8, 41.9, 30.2, 25.3.

For **5f**: ^{1}H NMR (acetone-d_6): $\delta = 6.21-5.98$ (m, 4H), 4.55−4.29 (m, OCH_2CF_3), 3.82−3.46 (m), 2.91, 2.82 (br s), 2.4 (br s), 1.91−1.82 (m), 1.45−1.19 (m), 0.52 (br s). ^{31}P NMR (acetone-d_6): $\delta = -6.27$ (s), −1.60 (d). ^{13}C NMR (acetone-d_6): $\delta =$ 138.15, 137.53, 137.02, 133.09, 124.03, 49.89, 45.47, 44.50, 44.17, 43.03, 42.99, 42.43, 42.30, 40.23, 64.22, 63.19, 62.80.

Preparation of the Cationic Initiator $[(CF_3CH_2O)_3P{=}NPCl_3]^+[PCl_6]^-$ (7). Phosphorus pentachloride (104.0 mg, 0.5 mmol, 2 equiv) was dissolved in 50 mL of CH_2Cl_2 over 1 h at 25 °C. To this solution was added 104.0 mg (0.25 mmol, 1 equiv) of the phosphoranimine $(CF_3CH_2O)_3P{=}NSiMe_3$, and the mixture was stirred at room temperature for 2−4 h. ^{31}P NMR spectroscopy of the reaction mixture indicated the presence of the desired product as evidenced by two doublets for the terminal PCl_3^+ and the $(CF_3CH_2O)_3P$ phosphorus atoms.

For **7**: ^{31}P NMR (D_2O): $\delta = 22.78$ ((d, $(CF_3CH_2O)_3P{=}N$), −9.91 (d, $Cl_3P{=}N$).

Typical Synthesis of Monotelechelic Polyphosphazenes from $[(CF_3CH_2O)_3P{=}NPCl_3]^+[PCl_6]^-$ (7). A solution of **7** was prepared as described above. Phosphoranimine **3** (1.12 g, 5 mmol, 20 equiv) was added to the solution, and the mixture was stirred at 25 °C for 2−24 h. After the conversion of phosphoranimine **3** to polymer **8** was complete, as indicated by ^{31}P NMR spectroscopy, 112 mg of compound **2a** (0.27 mmol, 1.1 equiv) was added to the reaction mixture, which was then stirred overnight. The reaction was considered complete when ^{31}P NMR spectroscopy showed the disappearance of the doublet at +8 ppm. All volatiles were removed from the reaction mixture under reduced pressure, and the resultant residue was dissolved in 10 mL of dry THF. Subsequent treatment of the reaction mixture with 3 mL of a 2.0 M solution of sodium trifluoroethoxide and purification by precipitation from THF into deionized water (3×) and hexanes (2×) yielded the hydrolytically stable monotelechelic polyphosphazene **9a**.

For **8**: ^{31}P NMR (D_2O): $\delta = 8.2$ (d, 1P), −12.46 (d, 1P), −14.5 (t, 2P), −15.5 (t, 2P), −17.6 (br s, 16P).

For **9a**: ^{1}H NMR (acetone-d_6): $\delta = 7.39$ (t, 3H), 7.25 (d, 2H), 4.21−4.56 (m). ^{31}P NMR (acetone-d_6): $\delta = -6.40$ (s), −4.65 (br s), −1.85 (d). ^{13}C NMR (acetone-d_6): 150.81, 135.78, 129.01, 128.91, 127.93, 127.64, 126.42, 123.96, 116.06, 64.11.

For **9b**: ^{1}H NMR (acetone-d_6): $\delta = 7.18$ (d, 2H), 6.91 (d, 2H), 4.22−4.56 (m), 3.77 (s, 6H). ^{31}P NMR (acetone-d_6): $\delta =$ −6.39 (br s), −4.61 (br s), −1.73 (d). ^{13}C NMR (acetone-d_6): 158.11, 145.25, 145.36, 123.79, 122.33, 115.25, 64.03, 55.71.

For **9c**: ^{1}H NMR (acetone-d_6): $\delta = 8.26-8.27$ (m, 2H), 7.94 (br s, 2H), 7.80 (d, 2H), 7.41−7.65 (m, 8H), 4.26−4.93 (m, OCH_2CF_3). ^{31}P NMR (acetone-d_6): $\delta = -6.32$ (s, −1.62 (d). ^{13}C NMR (acetone-d_6): 150.83, 135.88, 128.81, 128.62, 127.78, 127.45, 126.27, 124.03, 116.56, 64.18.

For **9d**: ^{1}H NMR ($CDCl_3$): $\delta = 4.24$ (q, 2H), 1.75 (t, 2H), 1.50 (s, 9H), 1.26 (t, 2H). ^{31}P NMR ($CDCl_3$): $\delta = -16.1$ (s). ^{13}C NMR ($CDCl_3$): $\delta = 123.4$, 63.1, 64.9, 32.0, 30.5, 28.7, 10.8.

For **9e**: ^{1}H NMR ($CDCl_3$): $\delta = 4.18$ (m, 4H), 3.55 (q, 4H), 1.43−1.55 (m, 4H), 1.33−1.36 (m, 2H), 0.86 (s, 9H), 0.06 (s, 6H). ^{31}P NMR ($CDCl_3$): $\delta = -8.83$. ^{13}C NMR ($CDCl_3$): $\delta =$ 124.3, 63.6, 60.4, 28.4, 44.2, 40.8, 31.2, 25.3.

For **9f**: ^{1}H NMR (acetone-d_6): $\delta = 6.11-5.96$ (m, 2H), 4.76−4.26 (m), 3.67−3.61 (m, 1H), 3.49−3.44 (m, 1H), 2.91 (br s, 1H), 2.82−2.79 (m, 2H), 2.40 (br s, 1H), 1.83−1.76 (m, 1H), 1.38−1.17 (m, 1H), 0.52−0.48 (br s, 1H). ^{31}P NMR (acetone-d_6): $\delta = -6.39$ (br s), −1.61 (d), −0.98 (d). ^{13}C NMR (acetone-d_6): $\delta = 137.68$, 137.31, 136.89, 132.99, 123.82, 49.54, 45.31, 44.25, 44.00, 42.87, 43.01, 42.21, 42.18, 40.21, 64.14, 63.01, 62.65.

For **9g**: ^{1}H NMR ($CDCl_3$): $\delta = 7.16$ (d, 4H), 6.93 (d, 4H), 6.58 (m, 1H), 5.58 (d, 2H), 5.11 (d, 2H), 4.18 (m, 4H). ^{31}P NMR ($CDCl_3$): $\delta = -8.45$. ^{13}C NMR ($CDCl_3$): $\delta = 150.23$, 136.78, 128.01, 127.21, 126.93, 126.54, 125.12, 123.02, 115.95, 65.31.

Acknowledgment. The authors thank the National Science Foundation for support of this work through Grant CHE-0211638. C.R.D. also thanks the Natural Sciences and Engineering Research Council of Canada (NSERC) for a Postdoctoral Research Fellowship.

References and Notes

(1) Allcock, H. R.; Lampe, F. W.; Mark, J. E. *Contemporary Polymer Chemistry*, 3rd ed.; Pearson Education, Inc.: New Jersey, 2003.
(2) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.
(3) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740.
(4) Allcock, H. R.; Nelson, J. M.; Prange, R.; Crane, C. A.; de Denus, C. R. *Macromolecules* **1999**, *32*, 5736.
(5) Nelson, J. M.; Primrose, A. P.; Hartle, T. J.; Allcock, H. R. *Macromolecules* **1998**, *31*, 947.
(6) Allcock, H. R.; Prange, R. *Macromolecules* **2001**, *34*, 6858.
(7) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Olshavsky, M. A. *Inorg. Chem.* **1999**, *38*, 280.
(8) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50.
(9) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Crane, C. A. *Macromolecules* **1997**, *30*, 2213.
(10) Nelson, J. M.; Allcock, H. R. *Macromolecules* **1997**, *30*, 1854.
(11) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Synth.* **1989**, *25*, 69.
(12) Prange, R.; Reeves, S. D.; Allcock, H. R. *Macromolecules* **2000**, *33*, 5763.
(13) The discrepancy between theoretical and experimentally obtained molecular weights is likely due to differences in hydrodynamic radii between the polyphosphazenes and the polystyrene standards.
(14) Allcock, H. R.; Laredo, W. R.; deDenus, C. R.; Taylor, J. P. *Macromolecules* **1999**, *32*, 7719.
(15) Allcock, H. R.; de Denus, C. R.; Prange, R. L.; Laredo, W. R. *Macromolecules* **2001**, *34*, 2757.
(16) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357.
(17) Colon, I.; Kelsey, D. R. *J. Org. Chem.* **1986**, *51*, 2627.
(18) Colon, I.; Kwiatkowski; G. T. *J. Polym. Sci.; Part A: Polym. Chem.* **1990**, *28*, 367.
(19) Lipshutz, B. H.; Pollart, D.; Monforte, J.; Kotsuki, H. *Tetrahedron Lett.* **1985**, *26*, 705.
(20) Prakash, C.; Saleh, S.; Blair, I. A. *Tetrahedron Lett.* **1989**, *30*, 19.

(21) Carpino, L. A.; Sau, A. C. *J. Chem. Soc., Chem. Commun.* **1979**, 514.
(22) Cunico, R. F.; Bedell, L. *J. Org. Chem.* **1980**, *45*, 4797.
(23) Corey, E. J.; Venkateswarlu, A. *J. Am. Chem. Soc.* **1972**, *94*, 6190.
(24) Kelly, D. R.; Roberts, S. M.; Newton, R. F. *Synth. Commun.* **1979**, *9*, 295.
(25) Matyjaszewski, K.; Moore, M. K.; White, M. L. *Macromolecules* **1993**, *26*, 6741.
(26) Allcock, H. R.; Powell, E. S.; Maher, A. E.; Berda, E. B., submitted for publication.
(27) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; John Wiley & Sons: New York, 2003.
(28) Montaudo, G.; Montaudo, M. S.; Samperi, F. In *Mass Spectrometry of Polymers*; Montaudo, G., Lattimer, R. P., Eds.; CRC Press: Boca Raton, FL, 2001; Chapter 10.

MA030554X