Synthesis of Trifluoromethyl- and Methylphosphazene Polymers: Differences between Polymerization and Initiator/Terminator Properties

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ABSTRACT: A new polyphosphazene, $[N{=}PPh(CF_3)]_n$, has been prepared via the PCl_5-induced cationic polymerization of $Me_3SiN{=}P(CF_3)(Ph)Br$. In addition, the cationic route has been used to produce $[N{=}PPh(Me)]_n$ with controlled molecular weights and narrow polydispersities. By contrast, the new monomer $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ failed to polymerize under any conditions but was used as an initiator and terminator to prepare both mono- and ditelechelic polymers. This monomer was also used to prepare $[F(Ph)(t\text{-}Bu)P{=}N(PCl_2{=}N)P(t\text{-}Bu)(Ph)F]^+$, which was used as a substrate for reactions with alkoxy and aryloxy groups to yield the hydrolytically stable materials, $[R(Ph)(t\text{-}Bu)P{=}N(PR_2{=}N)P(t\text{-}Bu)(Ph)R_2]$.

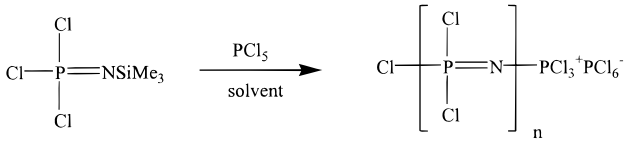
Introduction

The development of new synthetic methods for the production of polyphosphazenes, $(N{=}PR_2)_n$ with unique physical and chemical properties, is an important objective.[1−3] The various properties of these polymers are normally controlled by the side groups along the polymer backbone. Traditionally, most polyphosphazenes have been prepared by the thermal ring-opening and macromolecular substitution route developed in our program.[1] The initial step in this approach is the thermal ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, which yields the reactive macromolecular intermediate, poly(dichlorophosphazene), $(N{=}PCl_2)_n$.[1−3] Subsequent replacement of the chlorine atoms in $(N{=}PCl_2)_n$ with alkoxy, aryloxy, and/or amine nucleophiles has yielded several hundred different poly(organophosphazenes). However, this route allows for only minimal control of the molecular weight and generates polymers with broad polydispersities.[4]

Recently, these shortcomings were overcome through the discovery and development of an ambient temperature condensation synthesis of $(N{=}PCl_2)_n$. This synthetic method involves the living cationic-induced polymerization of $Me_3SiN{=}PCl_3$ (**1**) with trace amounts of PCl_5 (Scheme 1) to yield polymers with well-defined molecular weights and narrow polydispersities.[5] To date, the versatility of this living route has been extended to the synthesis of block copolymers,[6−10] star-branched polymers,[11] and end-functionalized polyphosphazenes.[3,12]

A major component of the current work in this area is directed toward the synthesis of polyphosphazenes with new side groups, including perfluorinated side groups. Efforts to incorporate perfluoroalkyl side groups into phosphazenes has long been a topic of serious study due to the expected hydrophobicity and unique solvent-repulsion characteristics of such species.[2,13−15] Several fluorine-containing polyphosphazenes, including $[N{=}P(OCH_2CF_3)_2]_n$ and $[N{=}P(OCH_2CF_3)(OCF_2(CF_2)_xCF_2H)]_n$,

Scheme 1



1 **2**

have been prepared and shown to possess interesting and unique properties such as elasticity, biocompatibility, and stability toward thermal degradation, oxidative cleavage, and organic solvents.[1] Although polymers of this type illustrate the importance of fluorinated groups in the generation of unique properties, they are limited by the presence of the P−O−C linkage and the presence of α-hydrogen atoms in the side groups. Thus, polyphosphazenes that contain an organic substituent directly attached to the backbone through a P−C bond form a class of polymers that are of special interest.

However, the synthesis of polyphosphazenes that contain direct P−C bonds has been a difficult barrier to overcome. The sensitivity of the N═P backbone bonds toward cleavage by alkyllithium and Grignard reagents makes the synthesis via macromolecular substitution of poly(dichlorophosphazene) difficult. Similarly, the thermal ring-opening polymerization of a variety of cyclotriphosphazenes such as $N_3P_3(R)Cl_5$ (R = Me, Et, *n*-Pr, *n*-Bu), $N_3P_3(R)_2Cl_4$ (R = Me, Et), and $N_3P_3(R)_3Cl_3$ (R = Me) produces polyphosphazenes with broad polydispersities.[16−19] Furthermore, the direct formation of fully substituted poly(organophosphazenes), $(N{=}PR_2)_n$, via the thermal ring-opening route is generally not achieved with fully substituted organophosphazene trimers, $(N{=}PR_2)_3$, unless a ring-strain-inducing transannular metallocene or similar unit is present on the trimer.[20−22]

The majority of polymers with direct P−C linkages are most easily prepared if alkyl or aryl groups are incorporated into a monomer before polymerization. The principal synthetic route to poly(organophosphazenes) of this type is via the condensation polymerization of *N*-silylphosphoranimines as developed by Neilson and Wisian-Neilson.[4,23−26] This polymerization proceeds, uncatalyzed, at temperatures near 180−200 °C, to produce

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a range of poly(aryl/alkylphosphazenes) with number-average molecular weights (M_n) that approach 10^5 and polydispersities of 1.5−3.0. In addition, recent reports describe the synthesis and characterization of phosphazene polymers in which the backbone phosphorus atom is part of an unsaturated heterocyclic hydrocarbon ring[24] or through the thermal decomposition of phosphazene azides, such as Ph(*o*-tolyl)PN_3.[27,28] However, these methods produce a limited number of polyphosphazenes with little to no molecular weight control.

In this paper, as part of our ongoing study of the cationic induced ambient temperature method,[5−13] we report the reactivity of the asymmetrically substituted monomers $Me_3SiN{=}P(CF_3)(Ph)Br$, $Me_3SiN{=}P(CH_3)(Ph)Br$, and $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ under cationic catalyzed conditions. The bromo-based monomers were synthesized following literature[25,29] procedures, while the $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ was obtained by a novel substitution reaction of the difluorophosphoranimine, $Me_3SiN{=}P(Ph)F_2$, with *tert*-butyllithium. The synthesis of the polyphosphazenes $[N{=}PPh(CF_3)]_n$ and $[N{=}PPh(CH_3)]_n$, via the PCl_5-induced polymerization of the respective bromo monomers, is reported here. In addition, the formation of linear short-chain oligomers $[R(Ph)(t\text{-}Bu)P{=}N(PR_2{=}N)P(t\text{-}Bu)(Ph)R_2]$ and mono- and ditelechelic polyphosphazenes using $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ as an initiating or terminating species is discussed.

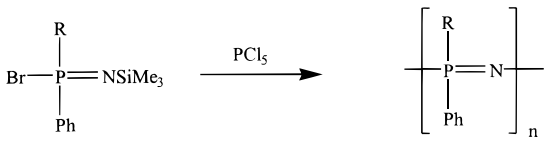
Results and Discussion

Overall Approach. The living cationic-induced polymerization of phosphoranimines is applicable to a wide range of derivatives that contain side groups with steric bulk and electron-withdrawing or -donating characteristics. With this in mind, it seemed possible that this route could be used to synthesize new polyphosphazenes with side groups that have traditionally been inaccessible. Of particular interest, and the focus of this paper, is the synthesis of perfluoromethyl, methyl, and *tert*-butyl-substituted materials. Additional interest was focused on the preparation of stereoregular polyphosphazenes, species only rarely reported in the past.[23−28]

Synthesis of Methyl- and Trifluoromethyl-Substituted Polyphosphazenes. Neilson, Wisian-Neilson, and their co-workers reported preliminary attempts to synthesize phosphazene systems containing trifluoromethyl and methyl substituents via the uncatalyzed condensation polymerizations of tris(organo)phosphoranimine species.[23,26,31,32] They found that thermal treatment (220 °C) of $Me_3SiN{=}P(Ph)(CF_3)(OCH_2CF_3)$ did not produce polymeric materials and that the monomer was recovered unchanged. Moreover, thermolysis of the monomers $Me_3SiN{=}P(CF_3)(Ph)Br$ (**3**) and $Me_3SiN{=}P(CH_3)(Ph)Br$ (**4**) gave mixtures of cyclic trimers and low molecular weight linear polymers.[33]

Previously, we have shown that $Me_3SiN{=}P(OCH_2CF_3)_2Br$ undergoes polymerization with trace amounts of PCl_5 in solution and in the bulk state at 35 °C, to produce $[N{=}P(OCH_2CF_3)_2]_n$ in moderate yield.[7] Thus, the polymerization behavior of $Me_3SiN{=}P(CF_3)(Ph)Br$ (**3**) and $Me_3SiN{=}P(CH_3)(Ph)Br$ (**4**) under similar conditions was explored. Phosphoranimines **3** and **4** were prepared according to literature procedures.[29,33,34] The polymerization reactions of **3** with PCl_5 in CH_2Cl_2 proceeded very slowly, and the monomer never fully polymerized. This is consistent with the behavior of other phenylorganophosphoranimines, such as $Me_3SiN{=}PPhX_2$ (X = Cl, F), where it has been observed that the solvent reacts with the monomer, initiator, and/or growing polymer chain to hinder the production of the desired polymer.[9] However, polymerizations of **3** in the bulk state at 35 °C proceeded to completion to yield polymers with controlled molecular weights. For example, the reaction of **3** with PCl_5 in a 20:1 ratio (Scheme 2) resulted in the rapid evolution of Me_3SiBr accompanied by a significant increase in the viscosity of the reaction mixture. The resultant viscous polymer was soluble in THF. Variations in the monomer-to-initiator ratio gave polymers with controlled molecular weights (Table 1, entries 1−3). [35]

Scheme 2



3: R = CF_3
4: R = CH_3

5: R = CF_3
6: R = CH_3

Table 1. Polymer Molecular Weights for the Polymerizations of 3 and 4 with PCl_5

			M_n		
polymer	monomer	M:I	found[a] ($\times 10^{-4}$)	calcd[b] ($\times 10^{-4}$)	PDI
5a	**3**	10:1	1.33	0.45	1.03
5b	**3**	20:1	1.65	0.83	1.02
5c	**3**	40:1	1.94	1.60	1.03
6a	**4**	5:1	0.20	0.19	1.19
6b	**4**	10:1	0.80	0.33	1.24
6c	**4**	20:1	1.31	0.61	1.21

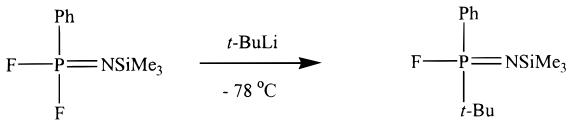
[a] Molecular weight obtained from GPC versus polystyrene standards following replacement of Br with $NaOCH_2CF_3$. [b] Calculated at 100% conversion.

Monomer **4** failed to polymerize in solution or in the bulk state over a 1 week period. However, polymerization did occur if the initiator $[Br(Ph)(CH_3)P{=}NPCl_3]^+[PCl_6]^-$ was first prepared in situ and the monomer was then added to it. In fact, the reactions of **4** with initiator ratios of 5:1 and 10:1 were complete within 12 h, as determined by ^{31}P NMR spectroscopy, while a 20:1 reaction took 4 times longer to reach completion. Before isolation of the polymers, all reaction mixtures were treated with sodium trifluoroethoxide to replace the halogen atoms by trifluoroethoxy groups. Each polymer (**6**) was isolated as a gum which was soluble in common organic solvents such as methylene chloride, THF, or chloroform. The polymers in this study, produced by the cationic method, were obtained under relatively mild conditions, with controlled molecular weights and low polydispersities.

New Synthetic Route to the Di(organo)monofluorophosphoranimine $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (8). The synthesis of asymmetric phosphoranimines has normally been achieved via the Wilburn method or through phosphorane routes.[29,32] Attempts have been reported to incorporate isopropyl and *tert*-butyl groups as part of a symmetrical (silylamino)phosphine $(Me_3Si)_2N{-}PR_2$ (R = *i*-Pr, *t*-Bu) via the reaction of monosubstituted chlorophosphines $(Me_3Si)_2N{-}P(R)Cl$ (R = *i*-Pr, *t*-Bu) with the appropriate Grignard or alkyllithium reagent.[4] However, this procedure was complicated by a variety of side reactions and did not produce the desired compound.

We have attempted the synthesis of a new target diorganomonofluorophosphoranimine containing a bulky

Scheme 3



7 **8**

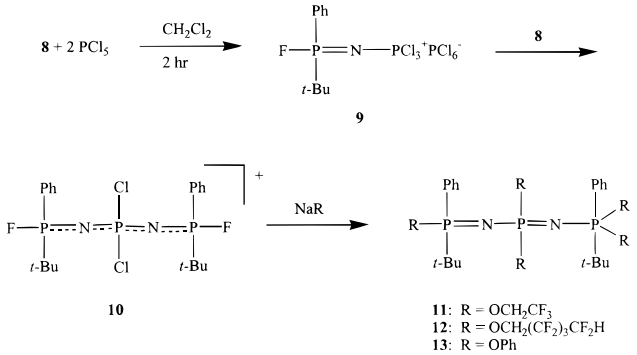
tert-butyl group, which was not attainable through the previously reported methods. The new approach utilizes the special reactivity of phosphorus−fluorine bonds. Cyclic trimeric and high polymeric phosphazene materials such as $(N{=}PF_2)_n$ have served as useful intermediates for the synthesis of a variety of alkyl-, aryl-, and organometallic-substituted polyphosphazenes.[36−39] The increased strength of the phosphorus−nitrogen bonds in $(N{=}PF_2)_n$, compared to their counterparts in $(N{=}PCl_2)_n$, results in an enhanced stability of the backbone toward Grignard and alkyllithium reagents. When these reagents are used to replace the chlorine atoms in $(N{=}PCl_2)_n$, a significant degree of skeletal cleavage occurs.[39−41] Thus, the present efforts focused on the reactions of organolithium reagents with $Me_3SiN{=}P(Ph)F_2$ (**7**) as a route to new asymmetric di(organo)phosphoranimines with P−C linkages.

Substitution reactions of stoichiometric amounts of the organolithium reagents MeLi, *n*-BuLi, and *t*-BuLi with $Me_3SiN{=}P(Ph)F_2$ at −78 °C were carried out in an effort to produce new monomers (Scheme 3). The reaction with *t*-BuLi gave the desired diorganomonofluorophosphoranimine, $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (**8**). However, it was found that the MeLi and *n*-BuLi reactions were not selective, and both of the fluorine atoms were replaced to produce the trisubstituted phosphoranimine species, $Me_3SiN{=}P(Ph)R_2$ (R = Me, *n*-Bu), as detected by ^{31}P NMR spectroscopy. The difference in reactivity of the lithium reagents suggests that the steric nature of the *t*-Bu group limits substitution to only one fluorine atom on the $Me_3SiN{=}P(Ph)F_2$ monomer. Thus, the substitution reactions of difluorophosphoranimine monomers serve as a versatile synthetic route to a variety of alkyl/aryl or organometallic phosphoranimines. In principle, monomer **8** is an excellent candidate for the cationic-induced polymerization process. Because of the absence of halogen leaving group, $Me_3SiN{=}P(Ph)Me_2$ and $Me_3SiN{=}P(Ph)(n\text{-}Bu)_2$ are not suitable for polymerization. They are, however, ideal candidates for the termination or initiation of living poly(dichlorophosphazene) polymer chains, similar to the various tris(organophosphoranimines) reported in a recent paper.[12]

Use of $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (8) as a Polymerization Initiator and Terminator. Monomer **8** with PCl_5, in various ratios, failed to polymerize in solution (CH_2Cl_2, toluene) or in the bulk state. Attempts to induce polymerization with the $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$ initiator were also unsuccessful. This resistance to polymerization is believed to be due to the effect of the electron-donating substituents and has been observed in similar diorganophosphoranimines.[7]

However, the inertness of monomer **8** toward polymerization allowed it to be utilized as an initiator or terminator for the preparation of both monotelechelic and ditelechelic polyphosphazenes.[12] Reaction between PCl_5 and **8** produced the short-chain initiator $[F(Ph)(t\text{-}Bu)P{=}NPCl_3]^+[PCl_6]^-$ (**9**). Treatment with 10 equiv of $Me_3SiN{=}PCl_3$ (**1**) gave a living poly(dichlorophosphazene) chain of formula $[F(Ph)(t\text{-}Bu)P{=}N{-}(Cl_2P{=}N)_n{-}PCl_3]^+[PCl_6]^-$, as monitored by ^{31}P NMR spectroscopy. The P−Cl bonds along the polymer backbone were then replaced by trifluoroethoxy groups to yield the monotelechelic polyphosphazene $Ph(t\text{-}Bu)(CF_3CH_2O)P{=}N[P(OCH_2CF_3)_2{=}N]_n(P(OCH_2CF_3)_4$. Similarly, a ditelechelic polymer was obtained by reaction of **1** with PCl_5 (10:1 molar ratio) in CH_2Cl_2 to produce $[(Cl_2P{=}N)_nPCl_3]^+[PCl_6]^-$. The living chain was terminated with 3 equiv of **8,** thereby quenching the polymerization. Subsequent replacement of the P−Cl bonds led to the isolation of the hydrolytically stable ditelechelic polymer $Ph(t\text{-}Bu)(CF_3CH_2O)P{=}N[P(OCH_2CF_3)_2{=}N]_n{-}P(OCH_2CF_3)_2(Ph)(t\text{-}Bu)$.

Scheme 4



Despite the fact that $[F(Ph)(t\text{-}Bu)P{=}NPCl_3]^+[PCl_6]^-$ initiates the polymerization of $Me_3SiN{=}PCl_3$, it cannot be used to polymerize $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (**8**) under similar conditions. Attempts to polymerize **8** from **9** using molar ratios of 5:1, 10:1, and 20:1 all resulted in the formation of a single product and unreacted monomer as indicated by ^{31}P NMR spectroscopy. The substitution pattern of the ^{31}P spectrum suggested that the product formed was the short-chain species $[F(t\text{-}Bu)(Ph)P{=}N{-}PCl_2{=}N{-}P(Ph)(t\text{-}Bu)F]^+$ (**10**), shown in Scheme 4, which was inert toward further reaction with **8**. Isolation of hydrolytically stable materials was achieved by replacement of the chlorine and fluorine atoms in compound **10** with alkoxy and aryloxy substituents. Specifically, the sodium salts of trifluoroethanol, octafluoropentanol, and phenol were used to prepare compounds **11**−**13**, as illustrated in Scheme 4. All products were characterized by mass spectrometry (FAB+) and multinuclear NMR spectroscopy.

Thus, the facile replacement of the chlorine and fluorine atoms in compound **10** suggests that it is feasible to prepare a wide variety of related compounds utilizing this methodology. For example, it may be possible to selectively replace the chlorine or fluorine atoms to yield materials with different properties. Similarly, the P−Ph units at the termini of these compounds are known to undergo nitration reactions and subsequent reduction to the free amines.[4] These materials may also be suitable candidates for a variety of condensation type polymerizations if two reactive functional groups are present as end units. These selective substitution reactions are currently under investigation.

Characterization of Polymers and Substituted Short-Chain Compounds. *Polymer **5**.* The bulk polymerization of monomer **3** yielded a viscous polymer which was analyzed by NMR and gel permeation chromatography (GPC). The ^{31}P NMR spectrum contained a quartet resonance at −10.4 ppm (J = 1050 Hz), which is consistent with the formation of the polymer

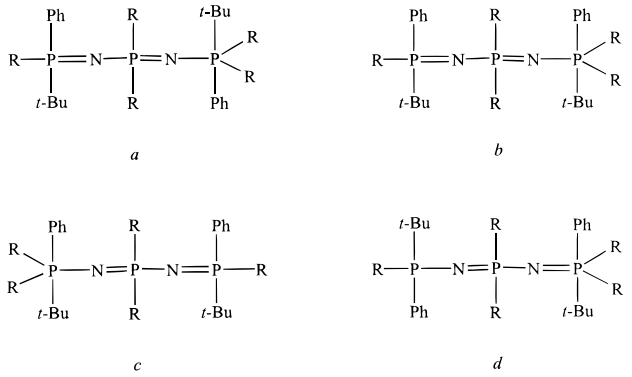


Figure 1. Four possible conformations for RPh(*t*-Bu)P=N−P(R$_2$)=N−P(*t*-Bu)(Ph)R$_2$.

[N=PPh(CF$_3$)]$_n$. Table 1 outlines the molecular weights of the polymers obtained at monomer **3** to PCl$_5$ ratios of 10:1 (**5a**), 20:1 (**5b**), and 40:1 (**5c**). A 100% conversion was assumed on the basis of the consumption of **3**. The difference between the calculated and found molecular weights is attributed to the discrepancies which are often observed when polyphosphazenes are compared to polystyrene standards.[35]

*Polymer **6***. Multinuclear NMR spectroscopy was employed to verify the structure of polymer **6**. The ^{31}P spectrum consisted of a broad singlet centered at 1.5 ppm for the [N=P(Ph)(Me)]$_n$ units, while the ^{1}H NMR spectrum contained several overlapping signals in the expected Ph, Me, and OCH$_2$CF$_3$ regions. Information on the stereoregularity of polymer **6** was obtained from ^{13}C NMR spectroscopy which indicated an atactic polymer with resolution of the triad structure. These NMR results are similar to those reported for **6** in the literature.[32] The molecular weights, determined by gel permeation chromatography, are listed in Table 1.[35]

Monotelechelic and Ditelechelic Polyphosphazenes. Monotelechelic and ditelechelic polyphosphazenes were isolated by the use of **8** as an initiator and terminator species and were characterized by multinuclear NMR and GPC. Values of $M_n = 6.2 \times 10^3$ and PDI = 1.34 were obtained for the monotelechelic material, while the ditelechelic material had a $M_n = 1.10 \times 10^4$ and PDI = 1.03. For both materials, the presence of the Ph and *t*-Bu end groups caused a change in the observed refractive index of the final polymer compared to that of [N=P(OCH$_2$CF$_3$)$_2$]$_n$ controls. The switching of the refractive index has previously been detected when block copolymers of [N=PPh(OCH$_2$CF$_3$)]$_m$[N=P(OCH$_2$CF$_3$)$_2$]$_n$ were prepared.[7−9]

*Compounds **10**−**13***. For the preparation of compound **10**, an equimolar reaction of initiator **9** with monomer **8** was carried out. The structure of this material was verified by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy as well as FAB+ mass spectrometry. The ^{31}P spectrum showed a doublet of doublets at 65 ppm and a triplet at −7.5 ppm in a 2:1 ratio, which is consistent with the structure of **10**. However, the ^{13}C NMR spectrum of this compound showed that the P−C(CH$_3$)$_3$ and P−Ph bonds on each end of the molecule were inequivalent with one another. This was attributed to the presence of *two distinct sets* of doublets of doublets in the appropriate regions of the spectrum.

Following substitution of the halogen atoms in **10**, the ^{1}H and ^{13}C NMR spectra became very complex. This was explained by the four possible structures that exist for a substituted material of this nature (Figure 1). ^{31}P NMR spectroscopy was used to verify that this was in fact the case. The ^{31}P resonances shifted downfield for the central [P(OR)$_2$] group and upfield for the terminal [P(Ph)(*t*-Bu)(OR)] and [P(Ph)(*t*-Bu)(OR)$_2$] units with respect to compound **10**. In all cases, the spectra were found to exhibit two doublets for the terminal phosphorus atoms and three doublets in a 1:2:1 ratio for the central [P(OR)$_2$] unit. This is explained by the structures shown in Figure 1, together with the fact that structures *b* and *c* are mirror images of each other and are thus indistinguishable on the NMR time scale.

Summary

The bromophosphoranimines **3** and **4** undergo cationic polymerization to yield the stereoregular polymers [N=P(Ph)(CF$_3$)]$_n$ (**5**) and [N=P(Ph)(CH$_3$)]$_n$ (**6**) with controlled molecular weights and low polydispersities. ^{13}C NMR spectroscopy was used to monitor the stereoregularity. The monomer Me$_3$SiN=P(Ph)F$_2$ underwent substitution reactions with alkyllithium reagents to produce both disubstituted Me$_3$SiN=P(Ph)R$_2$ (R = Me, *n*-Bu) and the new diorganomonofluorophosphoranimine Me$_3$SiN=P(*t*-Bu)(Ph)F (**8**). Monomer **8** was resistant to polymerization under a variety of conditions. However, it could be used as both an initiator and terminator in the preparation of mono- and ditelechelic polyphosphazenes. In addition, this monomer reacts with an equimolar ratio of PCl$_5$ to produce a new linear trimer (**10**) which readily undergoes substitution with alkoxy and aryloxy nucleophiles to produce **11**−**13** in good yields. These materials form a new class of asymmetric small molecule phosphazenes which may be useful as monomers for future polymerization processes.

Experimental Section

Materials. Sodium phenoxide, sodium trifluoroethoxide, sodium octafluoropentoxide, PhPF$_4$, Me$_3$SiN=P(Ph)(CF$_3$)Br (**3**),[29] Me$_3$SiN=P(CH$_3$)(Ph)Br,[33] and Me$_3$SiN=P(Ph)F$_2$,[29] were synthesized and purified by literature procedures. Phosphorus pentachloride, 1.7 M *tert*-butyllithium, 1.4 M methyllithium, 2.0 M *n*-butyllithium, octafluoropentanol, phenol, and 2,2,2-trifluoroethanol were obtained from Aldrich. Dichloromethane was dried and distilled from CaH$_2$ and then from P$_2$O$_5$ into the reaction flask. Tetrahydrofuran and hexane were distilled into the reaction flask from sodium benzophenone ketyl under an atmosphere of dry argon.

All glassware 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 ^{1}H spectra were recorded with a Bruker WM-360 NMR operated at 146, 90.27, and 360 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to 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. All NMR chemical shifts are reported in ppm while coupling constants are reported in hertz. 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 104 Å column, with the system calibrated versus polystyrene standards (Polysciences). The samples were eluted 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. FAB (+) and CI were collected on a Voyager DESTR spectrometer.

Preparation of Me$_3$SiN=P(Ph)(CF$_3$)Br (3). This monomer was synthesized by previously reported methods.[29] Additional characterization: ^{31}P NMR (CDCl$_3$): $\delta = -24.5$ (q; *J*

= 40). ^{1}H NMR ($CDCl_3$): δ = 7.8 (dd, J = 18, 7, 2H, *o*-C_6H_5), 7.5 (m, 3H, *m*-, *p*-C_6H_5), 0.19 (d, J = 3, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ = 137.6 (d, J = 178.1, 1C, quaternary C_6H_5), 132.5 (d, J = 20.4, 2C, C_6H_5), 129.1 (3C, C_6H_5), 128.7 (d of q, J = 320.5, 20.2, CF_3), and 3.2 (d, J = 30.9, $SiMe_3$).

Preparation of $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (8). To a THF solution (100 mL) of $F_2PhP{=}NSiMe_3$ (**5**) (10.1 g, 43.3 mmol) at −78 °C was added 1.7 M *t*-BuLi (25.5 mL, 43.3 mmol) dropwise over 5 min. The resultant slurry was allowed to warm to room temperature, and all volatiles were removed in vacuo. The viscous oil was distilled under vacuum (90 °C, 20 mmHg) to produce $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ as a clear colorless oil. The chemical shift for the ^{31}P NMR was 38.61 ppm, which is consistent with monomers that have electron-donating substituents attached to the phosphorus atom.

For (**8**): Yield 68% (7.8 g). ^{31}P NMR ($CDCl_3$): δ = 38.61 (d, J = 1031.7). ^{1}H NMR ($CDCl_3$): δ = 7.69−7.65 (m, 2H, C_6H_5), 7.41−7.18 (m, 3H, C_6H_5), 1.07 (d, J = 16.9, 9H, (CMe_3), and 0.00 ppm (s, 9H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): δ = 133.00 (d, J = 12.2, C_6H_4), 132.89 (d, J = 1.5, C_6H_5), 132.08 (d, J = 1.5, C_6H_5), 131.14 (d, J = 23.1, C_6H_5), 129.79 (d, J = 21.3, C_6H_5), 128.41 (d, J = 12.2, C_6H_5), 34.10 (dd, J = 104.1, 18.8, *C*Me_3), 24.97, 3.81 (d, J = 1.9, $SiMe_3$). MS (CI, Isobutane): m/z = 272 (MH^+, 100%), 255 (M − Me, 77%), and 200 (M − $SiMe_3$, 33%), in good agreement with isotopic abundance calculations.

Preparation of Polymer 5 from the PCl_5 −Induced Polymerization of $Me_3SiN{=}P(Ph)(CF_3)Br$ (3) in Solution. Treatment of **3** (0.343 g, 1.0 mmol) with PCl_5 (0.02 g, 0.10 mmol), in CH_2Cl_2 resulted in the slow, incomplete formation of the polymer (**5**) over 1 week. The progress of the reaction was monitored by ^{31}P NMR spectroscopy and by the presence of the ^{31}P NMR resonance for **3** at −24.5 ppm and new broad resonances at ca. − 10.4 ppm (J = 1043) for $[N{=}PPh(CF_3)]_n$. Moreover, attempted polymerization in other solvents such as cyclohexane, THF, and dioxane at various concentrations left the unreacted monomer with no indication of polymer formation.

Preparation of Polymer 5 from the PCl_5-Induced, Solvent-Free Polymerization of $Me_3SiN{=}P(Ph)(CF_3)Br$ (3). *General Procedure.* Solvent-free polymerizations of **3** (0.343 g, 1.0 mmol) with PCl_5 (0.02 g, 0.10 mmol) in a 10:1 ratio were performed in reaction vials under an inert atmosphere (Glove Box), with stirring at 35 °C. After 30 min the reaction mixture became immobile. At this point, THF (ca. 10 mL) was added to dissolve the rubbery material, and the solution was examined by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum showed the complete consumption of **3**, as evidenced by the disappearance of the ^{31}P NMR resonance for **3** at −24.5 ppm and the presence of new broad resonances at ca. −10.4 to − 3.7 ppm for $[N{=}PPh(CF_3)]_n$ (**5**). All volatile species were removed at reduced pressure. Polymer **5** was then precipitated into deionized water (3×) and hexane (2×). Yield 90%. ^{31}P NMR (CH_2Cl_2): δ = −10.4 ppm. GPC: $M_n = 1.33 \times 10^4$ and PDI = 1.03; T_g = −19 °C as observed by DSC. The molecular weights of **5** were controlled by variation of the **3** to PCl_5 ratios (Table 1).

For **5**: ^{31}P NMR ($CDCl_3$): δ = −10.4 (br. s). ^{1}H NMR ($CDCl_3$): δ = 7.98−7.73 (m, 4H, C_6H_5), 7.65−7.44 (m, 6H, C_6H_5), 4.61−4.19 (m, 6H, OCH_2CF_3). ^{13}C NMR ($CDCl_3$): δ = 139.53 (d, J = 76.4, quaternary C_6H_5), 138.98 (d, J = 74.5, C_6H_5), 135.62 (d, J = 91.3, C_6H_5), 131.14 (d, J = 11.3, C_6H_5), 130.72 (d, J = 13.4, C_6H_5), 129.76 (t, J = 17.2, C_6H_5), 123.64 (d of q, J = 187.0, 23.5, CF_3), 64.95−62.71 (OCH_2CF_3).

Procedure for the Polymerization of $Me_3SiN{=}P(CH_3)(Ph)Br$ (4). To a stirred solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (10 mL) at 20 °C was added $Me_3SiN{=}P(CH_3)(Ph)Br$ (0.065 g, 0.25 mmol) (**4**) quickly via syringe. The reaction mixture was stirred for 2 h at this temperature. ^{31}P NMR spectroscopy of the reaction mixture indicated the presence of the desired initiator species. To the reaction mixture was added a 5-, 10-, or 20-fold excess of $Me_3SiN{=}P(CH_3)(Ph)Br$, and the reaction was monitored by ^{31}P NMR until complete consumption of the monomer had taken place. At this time, a slight excess of 1.5 M sodium trifluoroethoxide was added to the reaction mixture to substitute the terminal bromine atoms. After stirring the reaction mixture at room temperature for 8 h, the volatiles were removed under reduced pressure. The residue was redissolved in methylene chloride and the polymer precipitated by the addition of hexanes. The positive ^{31}P NMR chemical shift of this polymer (2.04 ppm) is due to the electron-donating methyl substituent, in contrast to the electron-withdrawing CF_3 group in **5** which causes an upfield shift to −10.4 ppm.

For **6**: ^{31}P NMR ($CDCl_3$): δ = 2.04 (br s). ^{1}H NMR ($CDCl_3$): δ = 8.02−7.92 (m, 6H, C_6H_5), 7.46−7.31 (m, 4H, C_6H_5), 4.52−4.06 (m, 6H, OCH_2CF_3), 1.82−1.47 (several overlapping doublets, *Me*). ^{13}C NMR* ($CDCl_3$): δ = 140.48 (d, J = 72.6, C_6H_5), 139.57 (d, J = 92.6, C_6H_5), 138.05 (d, J = 72.5, quaternary C_6H_5), 130.62 (d, J = 10.3, C_6H_5), 129.21 (d, J = 10.7, C_6H_5), 127.26 (t, J = 12.0, C_6H_5), 62.32−60.01 (overlapping quartets, OCH_2CF_3), 22.49 (d, J = 92.4), 22.02 (d, J = 90.64), 21.44 (d, J = 92.4, Me).* OCH_2CF_3 carbons hidden under aromatic resonances.

Procedure for the Preparation of the Cationic Short-Chain Initiator $[FPh(t\text{-}Bu)P{=}NPCl_3]^+$ $[PCl_6]^-$ (9). To a stirred solution of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (10 mL) at 20 °C was added $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (0.068 g, 0.25 mmol) **(8)** quickly via syringe. The reaction mixture was stirred for 2 h at this temperature. ^{31}P NMR spectroscopy of the reaction mixture indicated the presence of the desired product as evidenced by a doublet of doublets for the terminal $FPh(t\text{-}Bu)P$ at 74.72 ppm (J = 1083, 21.8) and a triplet for the PCl_3^+ phosphorus atoms at 14.1 ppm (J = 12.1). The initiator solution was then used for further reactions without isolation.

Preparation of $Ph(t\text{-}Bu)(CF_3CH_2O)P{=}N[P(OCH_2CF_3)_2{=}N]_n{-}P(OCH_2CF_3)_4$. To a stirred solution of the initiator (**9**) in CH_2Cl_2 was added **1**. After 6 h, 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 $[Cl_2P{=}N]_n$. 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 $(Ph)(t\text{-}Bu)(CF_3CH_2O)P{=}N[P(OCH_2CF_3)_2{=}N]_n(P(OCH_2CF_3)_4$. This polymer was isolated via precipitation into deionized water (3×) and hexane (2×). ^{1}H NMR (acetone-d_6): δ = 7.93−7.96 (m, 3H, C_6H_5), 7.66−7.70 (m, 2H, C_6H_5), 4.33−4.73 (m, OCH_2-CF_3), 1.17−1.27 (m, 9H, CMe_3). ^{31}P NMR (acetone-d_6): −6.7 (br s, $[N{=}P(OCH_2CF_3)]_n$), −1.42 (br s, $P(OCH_2CF_3)_2(Ph)(t\text{-}Bu)$.

Preparation of $Ph(t\text{-}Bu)(CF_3CH_2O)P{=}N[P(OCH_2CF_3)_2{=}N]_n{-}P(OCH_2CF_3)_2(Ph)(t\text{-}Bu)$. 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 **1** 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 **8** was then added, and the solution was stirred for 8 h. All volatiles were removed under reduced pressure, and the di-end-capped poly(dichlorophosphazene) 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 $Ph(t\text{-}Bu)(CF_3$-$CH_2O)P{=}N[P(OCH_2CF_3)_2{=}N]_n{-}P(OCH_2CF_3)_2(Ph)(t\text{-}Bu)$was then recovered via precipitation into deionized water (3×) and hexane (2×). ^{1}H NMR (acetone-d_6): δ = 7.45−7.94 (m, 10H, C_6H_5), 4.20−4.62 (m, OCH_2CF_3), 1.03−1.28 (m, 18H, CMe_3). ^{31}P NMR (acetone-d_6): −6.7 (br s, $[N{=}P(OCH_2CF_3)]_n$), −1.42 (br s, $P(OCH_2CF_3)_2(Ph)(t\text{-}Bu)$.

Synthesis of $[FPh(t\text{-}Bu)P{=}N{-}P(Cl_2){=}N{-}P(t\text{-}Bu)(Ph)F]^+$ (10). This linear species was prepared in two different manners. Initially, the short-chain initiator, **9**, was reacted with $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (0.068 g, 0.25 mmol) and stirred for 2 h at 20 °C. ^{31}P NMR spectroscopy of the reaction mixture indicated the presence of the desired product. Alternatively, an equimolar reaction of PCl_5 (0.104 g, 0.5 mmol) in CH_2Cl_2 (10 mL) with $Me_3SiN{=}P(t\text{-}Bu)(Ph)F$ (0.136 g, 0.50 mmol) **(8)** at 20 °C could be employed. Removal of the solvents in vacuo allowed for the characterization of this air-sensitive material.

For **10**: ^{31}P NMR ($CDCl_3$): $\delta = 65.88$ (dd, $J = 1070$, 11.48, 2P, $P(C_6H_5)(t\text{-Bu})-$), -7.06 (t, $J = 11.66$, $-PCl_2-$). ^{1}H NMR ($CDCl_3$): $\delta = 7.73-7.76$ (m, 4H, C_6H_5), 7.59−7.66 (m, 6H, C_6H_5), 1.11 (d, $J = 19.5$, 18H, C*Me*$_3$). ^{13}C NMR ($CDCl_3$): $\delta =$ 135.60 (dd, $J = 9.8$, 1.49, C_6H_5), 132.08 (d, $J = 2.7$, C_6H_5), 131.14 (d, $J = 23.1$, C_6H_5), 129.79 (d, $J = 23.1$, C_6H_5), 128.41 (d, $J = 12.2$, C_6H_5), 34.10 (dd, $J = 104.1$, 18.83, *C*Me$_3$), 24.97, 3.81 (d, $J = 1.9$, $SiMe_3$). MS (FAB+): $m/z = 272$ (MH^+, 100%), 255 (M − Me, 77%), and 200 (M − $SiMe_3$, 33%), in good agreement with isotopic abundance calculations.

Synthesis of Compounds RPh(*t*-Bu)P═N−P(R$_2$)═N−P(*t*-Bu)(Ph)R$_2$ (11−13). General Procedure. Compound **10**, $[FPh(t\text{-Bu})P{=}N{-}P(Cl_2){=}N{-}P(t\text{-Bu})(Ph)F]^+$, was prepared as described above, and to the reaction mixture was added a 6-fold excess of the appropriate sodium salt ($NaOCH_2CF_3$ for **11**, $NaOCH_2(CF_2)_3CF_2H$ for **12**, and NaOPh for **13**) via syringe. The reaction mixture was then stirred overnight under an argon atmosphere to ensure complete substitution. The volatiles were removed, and the residue was redissolved in methylene chloride. The product was extracted with methylene chloride, washed with distilled water, and dried over magnesium sulfate. After filtration, solvent removal, and drying under vacuum, the products were obtained as yellow viscous oils or solids.

For **11**: yield: 76%. ^{31}P NMR ($CDCl_3$): $\delta = 40.55$ (d, 1P, $J = 35.4$, $P(t\text{-Bu})(C_6H_5)$), 40.44 (d, 1P, $J = 35.4$, $P(t\text{-Bu})(C_6H_5)$), −3.48 [(d, $J = 56.5$), −3.61 (d, $J = 56.0$), −3.73 (d, $J = 57.1$), 1P, $P(OCH_2CF_3)_2$]. ^{1}H NMR ($CDCl_3$): $\delta = 7.86-7.75$, 7.57−7.53, 7.49−7.40 (3m, 10H, C_6H_5), 4.76−4.61, 4.31−4.09 (2m, 10H, OCH_2CF_3), 1.25−1.09 (many overlapping doublets, 18H, C*Me*$_3$). ^{13}C NMR ($CDCl_3$): $\delta = 133.27$, 133.13, 132.60, 128.42, 128.28 (many overlapping doublets, C_6H_5), 63.16−60.85 (several overlapping quartets, OCH_2CF_3), 33.17−33.05; 34.37−34.20 (several signals, *C*Me$_3$), 23.75, 23.72, 23.62 (C*Me*$_3$). MS(FAB+): $m/z = 964$ (MH+, 3.7%), 703 (M − P(Ph)(*t*-Bu)-(OCH_2CF_3), 100%).

For **12**: yield: 82%. ^{31}P NMR ($CDCl_3$): $\delta = 52.81$ (d, 1P, $J = 44.6$, $P(t\text{-Bu})(C_6H_5)$), 52.67 (d, 1P, $J = 46.2$, $P(t\text{-Bu})(C_6H_5)$), −7.77 [(d, $J = 92.2$), −7.63 (d, $J = 91.4$), −7.49 (d, $J = 89.9$), 1P, $P(OCH_2(CF_2)_3CHF_2)_2$]. ^{1}H NMR ($CDCl_3$): $\delta = 7.70-7.49$ (m, 10H, C_6H_5), 6.18−5.81 (6 overlapping triplets, F_2CH, 5H), [4.46 (t, $J = 13.1$), 4.43 (t, $J = 13.2$), 3.90 (t, $J = 14.4$), 10H, OCH_2), 1.18−1.02 (several overlapping doublets, 18H, C*Me*$_3$). ^{13}C NMR ($CDCl_3$): $\delta = 135.25-129.31$ (several overlapping signals, C_6H_5), 121.59−120.13 (quaternary C_6H_5, overlapping signals), 118.37−104.74 (several overlapping triplets, CF_2, CF_2H), 63.65 (t, $J = 25.7$ Hz, OCH_2), 58.92 (t, $J = 25.4$ Hz, OCH_2), 34.84−33.66 (several overlapping doublets, *C*Me$_3$), 22.72 (C*Me*$_3$). MS(FAB+): $m/z = 1315$ ($MH+ - OCH_2CF_3$), 100%).

For **13**: yield: 85%. ^{31}P NMR (CD_2Cl_2): $\delta = 42.07$ (d, 1P, $J = 39.3$, $P(t\text{-Bu})(C_6H_5)$), 41.90 (d, 1P, $J = 40.7$, $P(t\text{-Bu})(C_6H_5)$), −18.94 [(d, $J = 75.5$), −19.11 (d, $J = 75.8$), −19.28 (d, $J =$ 78.6), 1P, $P(OPh)_2$]. ^{1}H NMR (CD_2Cl_2): $\delta = 7.61-6.68$ (m, 35H, C_6H_5), 1.27−0.86 (m, many overlapping doublets, 18H, C*Me*$_3$). ^{13}C NMR (CD_2Cl_2): $\delta = 158.54$ (quaternary C_6H_5), 150.99, 150.85 (quaternary C_6H_5), 133.70, 130.51, 129.74 (C_6H_5), 129.56, 126.48, 125.90, 121.07, 120.13 (C_6H_5), 119.20, 116.57 (C_6H_5), 35.70, 34.60 (*C*Me$_3$), 23.91, 23.84 (C*Me*$_3$). MS(FAB+): $m/z = 761$ (M − OPh, 53.2%).

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References and Notes

(1) Mark, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.
(2) *Contemporary Polymer Chemistry*; Allcock, H. R., Lampe, F. W., Eds.; Prentice Hall: Englewood Cliffs, NJ, 1992; p 546.
(3) Neilson, R. H.; Jinkerson, D. L.; Kucera, W. R.; Longlet, J. J.; Samuel, R. C.; Wood, C. E. *Inorganic and Organometallic Polymers*; ACS Symposium Series: Denver, 1994; Vol. 572, p 232.
(4) Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.
(5) Honeyman, C. H.; Manners, I.; Morrissey, C. T.; Allcock, H. R. *J. Am. Chem. Soc.* **1995**, *117*, 7035.
(6) Allcock, H. R.; Crane, C. A.; Morrissey, C. T.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1996**, *29*, 7740.
(7) Allcock, H. R.; Nelson, J. M.; Reeves, S. D.; Honeyman, C. H.; Manners, I. *Macromolecules* **1997**, *30*, 50.
(8) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Manners, I. Manuscript submitted for publication.
(9) Nelson, J. M.; Primrose, A. P.; Hartle, T. J.; Allcock, H. R.; Manners, I. *Macromolecules* **1998**, *31*, 947.
(10) Allcock, H. R.; Reeves, S. D.; Nelson, J. M.; Crane, C. A.; Manners, I. *Macromolecules* **1997**, *30*, 2213.
(11) Nelson, J. M.; Allcock, H. R. *Macromolecules* **1997**, *30*, 1854.
(12) Allcock, H. R.; Nelson, J. M.; Prange, R.; Crane, C. A.; de Denus, C. R. *Macromolecules* **1999**, *32*, 5736.
(13) Nelson, J. M.; Allcock, H. R.; Manners, I. *Macromolecules* **1997**, *30*, 3191.
(14) Bur, A. J. In *Fluoropolymers*; Wall, L. A., Ed.; Wiley: New York, 1972.
(15) Tesi, G.; Douglas, C. M. *J. Chem. Soc.* **1962**, 549.
(16) Allcock, H. R. In *The Chemistry of Inorganic Ring Systems*; Steudel, T., Ed.; Elsevier: Amsterdam, 1992; Chapter 9, p 145.
(17) Allcock, H. R. In *Ring-Opening Polymerization*; Brunelle, D. J., Ed.; Hanser: Munich, Germany, 1993; Chapter 7, p 217.
(18) Allcock, H. R. *Proceedings of Symposium on Catalysis*; ACS Symposium Series No. 496; American Chemical Society: Washington, DC, 1992; Chapter 18, p 236.
(19) Manners, I.; Riding, G. H.; Dodge, J. A.; Allcock, H. R. *J. Am. Chem. Soc.* **1989**, *111*, 3067.
(20) Allcock, H. R.; Dodge, J. A.; Manners, I.; Riding, G. H. *J. Am. Chem. Soc.* **1991**, *113*, 9596.
(21) Allcock, H. R.; Riding, G. H.; Manners, I.; McDonnell, G. S.; Dodge, J. A.; Desorcie, J. L. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1990**, *31*, 48.
(22) Cho, Y.; Back, H.; Sohn, Y. S. *Macromolecules* **1999**, *32*, 2167.
(23) Neilson, R. H.; Jinkerson, D. L.; Karthikeyan, S.; Samuel, R.; Wood, C. E. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1991**, *32*, 483.
(24) Gruneich, J. A.; Wisian-Neilson, P. *Macromolecules* **1996**, *29*, 5511.
(25) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.
(26) Neilson, R. H.; Wisian-Neilson, P. *Inorg. Synth.* **1989**, *25*, 69.
(27) Franz, U.; Nuyken, O.; Matyjaszewski, K. *Macromolecules* **1993**, *26*, 3723.
(28) Herring, D. L. *Chem. Ind. (London)* **1960**, 717.
(29) Wisian-Neilson, P.; Neilson, R. H.; Cowley, A. H. *Inorg. Chem.* **1977**, *16*, 1460.
(30) Honeyman, C. H.; Lough, A. J.; Manners, I. *Inorg. Chem.* **1994**, *33*, 2988.
(31) Wisian-Neilson, P.; Neilson, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 2848.
(32) Neilson, R. H.; Lee, C.-Y.; Cowley, A. H. *Inorg. Chem.* **1977**, *16*, 1455.
(33) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1980**, *19*, 1875.
(34) Wisian-Neilson, P.; Neilson, R. H. *Inorg. Chem.* **1982**, *21*, 3568.
(35) The discrepancy between theoretical and experimentally obtained molecular weights is thought to be because of an overestimation by gel permeation chromatography versus polystyrene standards.
(36) Allcock, H. R.; Evans, T. L. *J. Macromol. Sci., Chem.* **1981**, *A16* (1), 409.
(37) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.
(38) Allcock, H. R.; Patterson, D. B.; Evans, T. L. *J. Am. Chem. Soc.* **1977**, *99*, 6095.
(39) Allcock, H. R.; Patterson, D. B.; Evans, T. L. *Macromolecules* **1979**, *12*, 172.
(40) Harris, P. J.; Desorcie, J. L.; Allcock, H. R. *J. Chem. Soc., Chem. Commun.* **1981**, 852.
(41) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551.

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