Cationic Homo- and Copolymerization of Fluorophosphoranimines as an Ambient Temperature Synthetic Route to Poly(fluorophosphazenes), $[N{=}PF(R)]_n$, with Controlled Architectures

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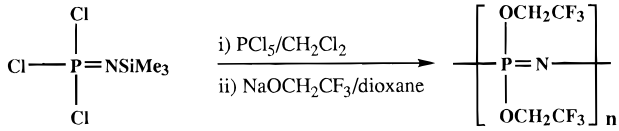
ABSTRACT: The PCl_5-induced polymerization of the fluorophosphoranimine $PhF_2P{=}NSiMe_3$ at ambient temperatures (35 °C) yields the poly(fluorophosphazene) $[N{=}PF(Ph)]_n$. This THF-soluble product was treated with an excess of sodium trifluoroethoxide in refluxing dioxane to replace the fluorine atoms by trifluoroethoxy groups and generate the known hydrolytically stable polymer $[N{=}PPh(OCH_2CF_3)]_n$. The molecular weights in this system can be controlled by variation of the monomer to initiator ratios, and polydispersities for $[N{=}PPh(OCH_2CF_3)]_n$ are in the range of 1.05−1.32. In order to explore the synthetic utility of $[N{=}PF(Ph)]_n$, the polymer was treated with Grignard or alkyllithium reagents such as MeLi, *n*-BuLi, or *p*-tolylmagnesium bromide to produce the poly(organophosphazenes) $[N{=}PPh(R)]_n$ (R = Me, *n*-Bu, *p*-tolyl). Complete replacement of the fluorine atoms using alkyl/aryllithium reagents induced a significant decline in molecular weights. However, treatment of $[N{=}PF(Ph)]_n$ with a 0.5 molar equiv of MeLi at −78 °C, followed by replacement of the remaining fluorine atoms with $NaOCH_2CF_3$ in refluxing dioxane, produced the mixed-substituent polyphosphazene $\{[N{=}PPh(OCH_2CF_3)_{0.5}(Me)_{0.5}]_y\}$ with $M_n = 2.4 \times 10^4$ (PDI = 1.10). The phosphoranimine $PhF_2P{=}NSiMe_3$ also reacts at 35 °C with "living" poly(dichlorophosphazene), $(N{=}PCl_2)_n$, to produce the block copolymer $\{[N{=}PCl_2]_n[N{=}PPh(F)]_m\}$. Halogen replacement by $NaOCH_2CF_3$ in refluxing dioxane produced the known hydrolytically stable block copolymer $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ with $M_n = 4.5 \times 10^4$ (PDI = 1.30).

Introduction

Recently we and our co-workers reported a new method for the preparation of poly(dichlorophosphazene), a crucial intermediate used for the preparation of approximately 700 different polyphosphazenes during the past 30 years.[1] This process involves the reaction of the phosphoranimine $Cl_3P{=}NSiMe_3$ (**1**) with small amounts of PCl_5 at 25 °C (Scheme 1).[2] The new approach permits the ambient temperature synthesis of poly(dichlorophosphazene), $(N{=}PCl_2)_n$, via a living cationic-induced polymerization, with molecular weight control.[3] Extensions of this method have included the direct production of a wide variety of poly(organophosphazenes) via the cationic-polymerization of *organo*phosphoranimines (e.g. **3,** Scheme 2),[4] the synthesis of phosphazene-based block copolymers[5] and the development of star-branched polyphosphazenes via the cationic polymerization of **1** with multifunctional initiators.[6]

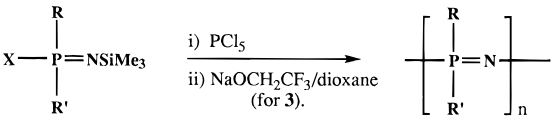
Another versatile intermediate for the synthesis of a variety of alkyl-, aryl- and organometallic-substituted polyphosphazenes is poly(difluorophosphazene), $(N{=}PF_2)_n$.[7−10] The greater strength of phosphorus−fluorine bonds in this polymer compared with phosphorus−chlorine bonds results in enhanced stability toward Grignard and alkyllithium reagents. When these reagents are used to replace the chlorine atoms in poly(dichlorophosphazene), $(N{=}PCl_2)_n$, a significant degree of skeletal cleavage occurs, accompanied by a decline in molecular weights at the stage of the final substituted polymers.[11,12]

Scheme 1



1 **2**

Scheme 2



3: R = Ph; R' = X = Cl
5: R = Me; R' = Et; X = Cl

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

The most common synthetic route to poly(fluorophosphazenes) involves the thermal ring-opening polymerization of cyclic species such as $(N{=}PF_2)_3$,[9,10,12,13] $[N_3P_3(R)F_5]$ {R = Me, Et, n-Pr, t-Bu, Ph, $(C_5H_4)Fe(C_5H_5)$}[14−18] and *transannular*-$[N_3P_3F_4(C_5H_4)_2Fe]$[19,20] at temperatures in the range 250−350 °C, to yield the corresponding polyphosphazene species $(N{=}PF_2)_n$, $[N{=}P(R)F\{N{=}PF_2\}_2]_n$ and $[(N{=}PF_2)\{N{=}PF(C_5H_4)\}_2Fe]_n$, but without molecular weight control and with broad polydispersities.

In this paper, as part of our ongoing study of the scope of the cationic induced ambient temperature method,[2,3] we report an alternative approach to the synthesis of poly(fluorophosphazenes). These polymerizations take place at ambient temperatures, allow for molecular

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Table 1. Polymer Molecular Weights for the PCl_5-Induced Polymerizations of 3 and 7 under Solvent-Free Conditions

monomer	M:I	reaction time, h	M_n ($\times 10^{-4}$) found[a]	M_n ($\times 10^{-4}$) calculated[b]	PDI
3[c]	10:1	6	1.5[c]	0.44	1.03
7	10:1	0.5	1.2	0.44	1.08
7	20:1	1	1.8	8.8	1.05
7	40:1	3	3.8	1.8	1.28
7	80:1	8	4.3	3.5	1.32

[a] Molecular weights by GPC following replacement of Cl by $NaOCH_2CF_3$. [b] Calculated at 100% conversion. [c] From ref 5.

weight control, and provide polymers with narrow polydispersities.

Results and Discussion

Overall Approach. Initial reactivity studies with the phosphoranimine species $Cl_3P{=}NSiMe_3$ (**1**) revealed that stoichiometric reactions of **1** with PCl_5 produce the short chain cationic species $[Cl_3P{=}N{-}PCl_3]^+$ $[PCl_6]^-$.[2,21] The addition of small quantities of PCl_5 to **1** resulted in the quantitative formation of poly(dichlorophosphazene), both in solution and in the bulk state.[2] After chlorine replacement with $NaOCH_2CF_3$, these species yielded the hydrolytically stable trifluoroethoxy derivative $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) with controlled molecular weights and narrow polydispersities. This "living" cationic, ambient temperature method has recently been applied to a variety of mono- and di*organo*phosphoranimines to bring about the direct synthesis of poly(organophosphazenes). Alkyl/arylphosphoranimines such as $PhCl_2P{=}NSiMe_3$ (**3**) and $Me(Et)ClP{=}NSiMe_3$ (**5**) undergo PCl_5 induced polymerizations at 35 °C under solvent-free conditions to produce polyphosphazenes with controlled molecular weights and low polydispersity indices.[4] The ambient temperature PCl_5-induced cationic polymerization is applicable to a wide range of phosphoranimines that contain side groups with steric bulk and electron-withdrawing or electron-donating characteristics (Scheme 2). In view of the known synthetic utility of poly(fluorophosphazenes) we have explored the possibility that the "living" cationic, ambient temperature route can be applied to fluorine-containing monomers as a method for the direct synthesis of poly(fluorophosphazenes). The fluorophosphoranimine $PhF_2P{=}NSiMe_3$ (**7**), was chosen as an example to probe this possibility. This monomer was found to undergo a "living" ambient temperature cationic polymerization under several different sets of conditions. A summary of representative reaction conditions and molecular weight data for these polymerizations is shown in Table 1.

Synthesis and Polymerization of the Phosphoranimine $PhF_2P{=}NSiMe_3$ (7). Fluorinated phosphoranimines $R_nF_{3-n}P{=}NSiMe_3$ (R = F, alkyl, aryl; n = 1, 2) were required for use in the PCl_5-induced polymerizations. The plan was to polymerize these monomers using the techniques developed for *organo*phosphoranimines in our earlier work with $PhCl_2P{=}NSiMe_3$ (**3**) and $Me(Et)ClP{=}NSiMe_3$ (**5**). In the late 1970s, Neilson, Wisian-Neilson and Cowley reported the synthesis of the fluorinated phosphoranimine $PhF_2P{=}NSiMe_3$ (**7**), via the reaction of $PhPF_4$ with $LiN(SiMe_3)_2$ in hexane,[22] thus providing a suitable monomer for these polymerization studies.

Polymerization reactions with **7** in CH_2Cl_2 solutions proceeded very slowly and not to completion. This was similar to the previously reported polymerization activity of $PhCl_2P{=}NSiMe_3$ (**3**) with PCl_5 in solution.[4] For example, treatment of **7** with PCl_5 in a 20:1 ratio in CH_2Cl_2 resulted in a 50% conversion to $[N{=}PPh(F)]_n$ over 1 week as monitored by ^{31}P NMR spectroscopy. Thus, subsequent polymerization attempts were performed under solvent-free conditions at 35 °C, as described earlier for the PCl_5-induced polymerization of a series of organophosphoranimines (see Scheme 2).[4] Reaction of **7** with PCl_5 in a 20:1 ratio in the bulk state at 35 °C with stirring, resulted in the rapid evolution of Me_3SiF accompanied by a significant increase in the viscosity of the reaction mixture. Reactions were carried out in capped vials in which a significant pressure buildup occurred following addition of PCl_5 to the monomer. The 20:1 **7**:PCl_5 mixture became immobile after 1 h. The resultant rubbery residue dissolved in THF and was shown by ^{31}P NMR spectroscopy to possess broad doublet resonances at ca. 10.4−3.7 ppm ($^2J_{P-F}$ = 972 Hz), consistent with the formation of $[N{=}PPh(F)]_n$. Similar ^{31}P NMR spectra and coupling constants have been observed for other partially substituted poly(fluorophosphazenes) $[N{=}PF(R)]_n$ (R = Ph, OCH_2CF_3 NHMe, NHBu, NMe_2, NHC_6H_5).[13,23] The reaction solution was then treated with $NaOCH_2CF_3$ to produce the known macromolecule $[N{=}PPh(OCH_2CF_3)]_n$ (**4**) with an M_n of 1.8×10^4 (PDI = 1.05) as determined by GPC analysis. Thus, the PCl_5-induced polymerization of **7** in the bulk state at 35 °C results in an increased polymerization activity compared with reaction in solution.

The polymer chains remained active after all the initial monomer **7** had been consumed. For example, a sample of $[N{=}PPh(F)]_n$ was prepared via the reaction of **7** with PCl_5 in a 20 :1 ratio under conditions where all the phosphoranimine had been converted to polymer, as determined by ^1H and ^{31}P NMR spectroscopy. A portion of this mixture was treated with $NaOCH_2CF_3$ to produce a sample of polymer **4** which was shown by GPC analysis to have an $M_n = 1.8 \times 10^4$ and PDI = 1.08. Further addition of phosphoranimine **7** to the remaining polymerization mixture (to generate a molar ratio of **7**:$[N{=}PPh(F)]_n$ of 4:1) resulted in the continued conversion of **7** to polymer over 24 h. After fluorine replacement by reaction with $NaOCH_2CF_3$, GPC analysis of the polymer **2** formed from this reaction revealed a higher molecular weight component having $M_n = 4.6 \times 10^4$ and PDI = 1.39 (Figure 1), with no trace remaining of the initial lower molecular weight fraction. Thus, it appears that the active chain ends can resume chain growth following the addition of more monomer, as reported previously for the cationic induced polymerizations of $Cl_3P{=}NSiMe_3$ (**1**) and $Me(Et)ClP{=}NSiMe_3$ (**5**).[2−4]

The molecular weights in the PCl_5-induced polymerization of **7** can be controlled by variations of the monomer:initiator ratios as outlined in Table 1. As reported previously for the cationic polymerization of *organo*phosphoranimines, increases in the monomer:initator ratio are accompanied by increased polydispersities.[4] Interestingly, the fluorinated monomer **7** polymerizes more rapidly than does the analogous chlorinated monomer **3** under identical conditions. This enhanced reactivity is surprising considering the greater strength of phosphorus−fluorine bonds vs phosphorus−chlorine bonds. Perhaps the smaller van der Waals radius of fluorine (1.35 Å, cf; Cl = 1.80 Å) allows the polymeri-

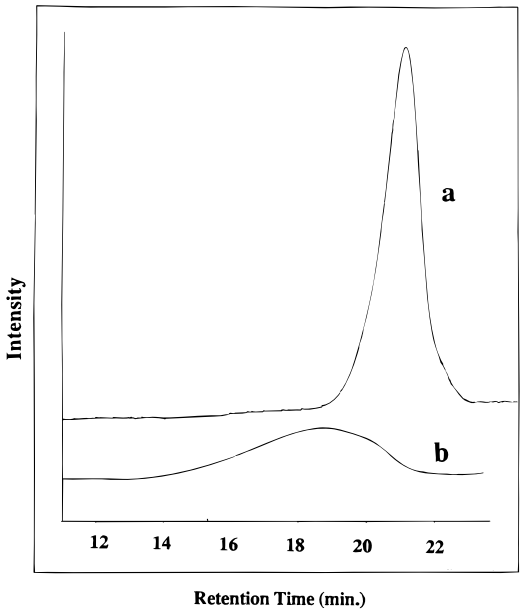


Figure 1. Activity of polymer chains. GPC chromatograms of polymer **4** (a) formed via the initial 20:1 **7**:PCl_5 ratio and (b) formed upon further addition of phosphoranimine **7**.

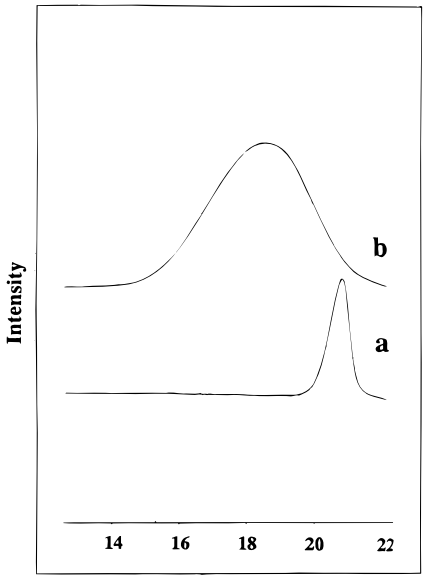


Figure 2. GPC chromatograms of: (a) the initial homopolymer **4** formed via reaction of **1** with PCl_5, and (b) the reaction after addition of **7** to a "living" sample of $(N{=}PCl_2)_n$, resulting in the formation copolymer **10** .

zation of **7** to proceed more rapidly than its chlorinated analog **3**.

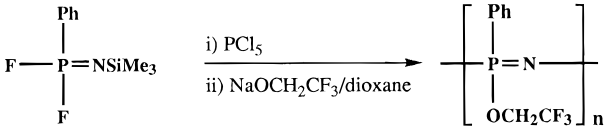
Copolymerization of $Cl_3P{=}NSiMe_3$ (1) with $PhF_2P{=}NSiMe_3$ (7). Synthesis of Polyphosphazene Block Copolymers. Recently, we described the ambient temperature synthesis of polyphosphazene block copolymers via the living cationic polymerization of phosphoranimines.[5] This new route provides phosphazene block copolymers with controlled molecular weights and narrow polydispersities. This synthetic approach involves the reaction of the phosphoranimines $PhCl_2P{=}NSiMe_3$ (**3**) and $Me(Et)ClP{=}NSiMe_3$ (**5**) with "living" samples of $[N{=}PCl_2]_n$, produced via reaction of $Cl_3P{=}NSiMe_3$ (**1**) with PCl_5. This procedure results in the synthesis of phosphazene block copolymers of types $\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$ (**8**) and $\{[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ (**10**). Macromolecular substitution of these species with sodium trifluoroethoxide to replace the reactive chlorine atoms with trifluoroethoxy groups produces the hydrolytically stable species $(\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**9**) and $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe(Et)]_m\}$ (**11**). The macromolecular substitution of the intermediate copolymers **8** and **10** can be extended to allow for a variety of derivative polymers to be synthesized.[24] Although large numbers of phosphazene polymers have been synthesized by the macromolecular nucleophilic substitution of poly(dichlorophosphazene), phosphazene block copolymers that can be tailored by variation of side groups through the macromolecular substitution method have not been reported before. As part of this approach, the incorporation of fluorinated phosphazene segments into block copolymers may impart unique substitution patterns due to the different reactivity of fluorophosphazenes vs chlorinated polyphosphazenes. Thus, attempts to initiate the fluorophosphoranimine $PhF_2P{=}SiMe_3$ (**7**) with "living" samples of $[N{=}PCl_2]_n$ were undertaken to synthesize partially fluorinated polyphosphazene block copolymers.

Reaction of **1** with PCl_5 in a 20:1 ratio in CH_2Cl_2 at 25 °C resulted in the formation of $(N{=}PCl_2)_n$ over the time span of 4 h. A portion of this reaction mixture was treated with $NaOCH_2CF_3$, to produce $[N{=}P(OCH_2CF_3)_2]_n$ (**2**) with an M_n of 2.0×10^4 (PDI = 1.01 by GPC). To the remaining portion of $(N{=}PCl_2)_n$ was added the phosphoranimine $PhF_2P{=}NSiMe_3$ (**7**) (in a 3:1 ratio with respect to **1**), and the reaction temperature was increased to ca. 35 °C. This resulted in the polymerization of **7** to form $\{[N{=}PCl_2]_n[N{=}PF(Ph)]_m\}$ (**12**) as monitored by ^{31}P NMR spectroscopy over a span of 24 h. Subsequent treatment of this reaction mixture with $NaOCH_2CF_3$ in refluxing dioxane replaced the reactive halogen atoms by trifluoroethoxy groups. GPC analysis of this macromolecule revealed an M_n of 4.5×10^4 (PDI = 1.30), consistent with the formation of the block copolymer $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**10**) (Figure 2). The refractive index of the GPC peak for **10** was found to be of opposite polarity to that found for **2**, and this is consistent with previously reported GPC analyses of polyphosphazene block copolymers.[5,24,25] ^{31}P NMR spectroscopy indicated the presence of characteristic peaks for both $[N{=}PPh(OCH_2CF_3)]_m$ at 3.1 ppm and $[N{=}P(OCH_2CF_3)_2]_n$ at −6.9 ppm which integrate in a 1.2:1 ratio. This is consistent with the GPC estimates for the size of the corresponding blocks.

Investigations are now in progress to study the different reactivities of the P−F and P−Cl bonds in these copolymers in order to develop a pathway for the selective substitution of the different halogen atoms. This could yield block copolymers with unique combinations of properties.

Reactivity of $[N{=}PF(Ph)]_n$ toward Alkyl/Aryllithium and Grignard Reagents. Previous reactivity studies of the replacement of fluorine in poly(fluorophosphazenes) by organic groups via reaction with organolithium reagents showed that the fluorinated polymers are more resistant to side reactions than are their chlorophosphazene analogs.[8,10,13,23] For example, poly(difluorophosphazene), $(N{=}PF_2)_n$, reacts with phenyllithium to replace up to 70% of the fluorine atoms, followed by treatment with $NaOCH_2CF_3$ to produce $[N{=}PPh_{0.7}(OCH_2CF_3)_{0.3}]_n$ without appreciable polymer backbone cleavage (M_w ca. 1×10^6). However, the molecular weights of fully phenylated phosphazenes $(N{=}PPh_2)_n$, synthesized by this macromolecular substi-

Scheme 3



7 **4**

tution reaction, are considerably lower ($M_w = (5-8) \times 10^4$) than those of the partially phenylated derivatives. Similar reactions of $(N{=}PF_2)_n$ with varying ratios of methyl- or *n*-butyllithium produced cross-linked polyphosphazenes or low molecular weight polymers.[10] These macromolecular substitution reactions were also complicated by the fact that poly(difluorophosphazene) is soluble only in perfluorinated solvents, media in which most organolithium reagents are insoluble, thus producing a heterogeneous reaction mixture. Thus, the new synthetic route to fluorinated phosphazenes, such as $[N{=}PF(Ph)]_n$, and the solubility of this species in common organic solvents, allowed the reactivity of this polymer with organolithium and Grignard reagents to be examined.

Samples of $[N{=}PF(Ph)]_n$ were synthesized via treatment of **7** with PCl_5 in a 20:1 ratio under solvent-free conditions. Portions of each sample (ca. 10%) were treated with $NaOCH_2CF_3$ to produce $[N{=}PPh(OCH_2CF_3)]_n$ (**4**) (Scheme 3) which, by analysis by GPC, showed that these macromolecules possesed molecular weights (M_n) of 1.8×10^4 (PDI = 1.06). The remainder of the $[N{=}PF(Ph)]_n$ samples were treated with stoichiometric amounts of MeLi, *n*-BuLi, and tolylmagnesium bromide respectively at −78 °C in THF, with reaction times of ca. 45 min in each case. These reactions produced the known organophosphazenes $[N{=}PPh(Me)]_n$ (**13**),[26] $[N{=}PPh(Bu)]_n$ (**14**),[10] and $[N{=}PPh(tolyl)]_n$ (**15**),[27] respectively. When stoichiometric amounts of the nucleophiles interacted with $[N{=}PF(Ph)]_n$, a significant decline in polymer molecular weight occurred as detected by GPC analysis of the poly(organophosphazenes). Polymers **13**−**15** had M_n values of $(5.4-5.6) \times 10^3$, which are an order of magnitude lower than the samples that were treated with $NaOCH_2CF_3$ only. Similar behavior was found for the interactions of poly(difluorophosphazene) with alkyllithium reagants at high loadings (ca. 70%).[8,10] However, reaction of $[N{=}PF(Ph)]_n$ (synthesized via treatment of **7** with PCl_5 in a 40:1 ratio under solvent-free conditions) with 0.5 molar equiv of MeLi at −78 °C, followed by replacement of the remaining fluorine atoms with $NaOCH_2CF_3$ in refluxing dioxane, produced the mixed-substituent polymer $\{[N{=}PPh(OCH_2CF_3)_{0.5}(Me)_{0.5}\}$ (**16**). The identity of this polymer was confirmed by ^{13}C, ^{1}H, and ^{31}P NMR spectroscopy. A portion of the initial $[N{=}PF(Ph)]_n$ sample, before reaction with MeLi, was treated with $NaOCH_2CF_3$ to produce $[N{=}PPh(OCH_2CF_3)]_n$ (**4**) which by GPC analysis was found to possess an M_n of 5.5×10^4 (PDI = 1.26). The mixed-substituent polymer **16** was found to possess an M_n of 2.4×10^4 (PDI = 1.10, by GPC). By similar methods, a mixed-substituent species $\{[N{=}PPh(OCH_2CF_3)_{0.25}(Me)_{0.75}\}$ (**17**) ($M_n = 2.3 \times 10^4$, PDI = 1.04, by GPC) was synthesized by treatment of 0.75 molar equiv of MeLi with $[N{=}PF(Ph)]_n$, itself synthesized by treatment of **7** with PCl_5 in a 40:1 ratio under solvent free conditions (cf. $[N{=}PPh(OCH_2CF_3)]_n$ (**4**) $M_n = 2.7 \times 10^4$, PDI = 1.16). Thus, partial fluorine replacement of $[N{=}PF(Ph)]_n$ by MeLi is possible without a significant degree of backbone cleavage or cross-linking. This is in contrast to the methylation attempts carried out with $(N{=}PF_2)_n$. Perhaps the presence of a bulky phenyl substituent at each phosphorus atom along the polymer chain sterically protects the phosphazene backbone from attack and subsequent cleavage.

Summary

The "living" cationic polymerization of phosphoranimines as an ambient temperature route to polyphosphazenes has been employed for the synthesis of phosphazenes with direct phosphorus−fluorine bonds. Initiation of the fluorophosphoranimine $PhF_2P{=}NSiMe_3$ (**7**) with small quantities of PCl_5 under solvent-free conditions at 35 °C produces $[N{=}PF(Ph)]_n$ with controlled molecular weights and narrow polydispersities. This reactive intermediate serves as a versatile precursor to alkyl/aryl-substituted phosphazenes via reactions with metalloorganic reagents in THF solutions. However, stoichiometric reactions of $[N{=}PF(Ph)]_n$ with MeLi, *p*-tolylmagnesium bromide, and *n*-BuLi result in some polymer backbone cleavage and molecular weight decline. By contrast, partial fluorine replacement (ca. 50−75%) occurs with only minor backbone cleavage and without appreciable cross-linking. The phosphoranimine $PhF_2P{=}SiMe_3$ (**7**) also undergoes coupling reactions with "living" samples of poly(dichlorophosphazene), $(N{=}PCl_2)_n$, to produce the block copolymer $\{[N{=}PCl_2]_n[N{=}PPh(F)]_m\}$ (**12**). This species may serve as an important intermediate in the preparation of block copolymers with hitherto inaccessible properties. The different reactivities of fluorine and chlorine atoms linked to a polyphosphazene chain open up avenues for the controlled substitution of different regions of the polymer. For example, the formation of separate hydrophobic and hydrophilic regions is of interest in surface science and in composite structures. These possibilities are currently being explored.

Experimental Section

Materials and Equipment. Sodium trifluoroethoxide,[28] $PhPF_4$ $Cl_3P{=}NSiMe_3$,[2,3,21,29] and $PhF_2P{=}NSiMe_3$[22] were synthesized and purified by literature procedures. The 1.0 M tolylmagnesium bromide, 1.6 M *n*-butyllithium and 1.4 M methyllithium were obtained from Aldrich. 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. ^{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 an internal $CDCl_3$. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, American Polymer Standards AM gel 10 mm, and AM gel 10 mm 10^4 Å column, with the system calibrated vs polystyrene standards (Polysciences). The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv).

Preparation of $PhF_2P{=}NSiMe_3$ (7). This monomer was synthesized by previously reported methods.[22] Additional characterization was as follows. ^{31}P-NMR ($CDCl_3$): $\delta = -4.5$ ppm (t; $^2J_{P-F} = 1075$ Hz). MS (CI, isobutane): $m/z = 234$ (MH^+, 100%), 218 ($M^+ - Me$, 45%), in good agreement with isotopic abundance calculations.

PCl_5-Induced Polymerization of $PhF_2P{=}NSiMe_3$ (7) in Solution. Treatment of **7** (0.22 g, 1.0 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in a 10:1 ratio, in CH_2Cl_2, resulted in the slow, incomplete formation of the polymer $[N{=}PF(Ph)]_n$ 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 **7** at −4.5 ppm and new broad resonances at ca. 10.4−3.7 ppm ($^2J_{P-F}$ = 972 Hz) for [N=PPh(F)]$_n$.

PCl_5-Induced, Solvent-Free Polymerization of $Ph-F_2P=NSiMe_3$ (7). General Procedure. Solvent-free polymerizations of **7** (0.20 g, 0.86 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol) in a 10:1 ratio were performed in reaction vials under an inert atmosphere (glovebox), with stirring at 35 °C. After 30 min the reaction mixture becomes 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 **7**, as evidenced by the disappearance of the ^{31}P NMR resonance for **7** at −4.5 ppm and the presence of new broad resonances at ca. 10.4−3.7 ppm ($^2J_{P-F}$ = 972 Hz) for [N=PPh(F)]$_n$. All volatile species were removed at reduced pressure. The residue was then dissolved in 10 mL of dioxane and treated with 2.5 M sodium trifluoroethoxide (10 mmol) in dioxane (4 mL). The mixture was then refluxed for 48 h to produce the known macromolecule [N=P(Ph)(OCH_2CF_3)]$_n$ (**4**). Polymer **4** was then precipitated into deionized water (3x) and hexane (2×).

For **4**: Yield 90%. ^{31}P-NMR (CH_2Cl_2): δ = 3.1 ppm.[27] GPC: $M_n = 1.2 \times 10^4$ and PDI = 1.08.

The molecular weights of **4** were controlled by variation of the **7**:PCl_5 ratios. The reactions were carried out under solvent-free conditions at 35 °C with (i) a 20:1 ratio of **7** (0.40 g, 1.72 mmol) with PCl_5 (ca. 0.02 g, 0.09 mmol), (ii) a 40:1 ratio of **7** (0.8, 3.44 mmol) to PCl_5 (0.02 g, 0.09 mmol), and (iii) a 80:1 ratio of **7** (1.6, 6.88 mmol) to PCl_5 (0.02 g, 0.09 mmol). In the case of i−iii, the polymerization times and molecular weights for **4** after replacement of the fluorine atoms by sodium trifluoroethoxide were as follows: (i) 1 h, GPC, $M_n = 1.8 \times 10^4$, and PDI = 1.05; (ii) 3 h, GPC, $M_n = 3.9 \times 10^4$, and PDI = 1.28; (iii) 8 h, GPC, $M_n = 4.3 \times 10^4$, and PDI = 1.32.

Copolymerization Reactions of $PhF_2P=NSiMe_3$ (7) with $Cl_3P=NSiMe_3$ (1). To a strirred solution of PCl_5 (ca. 20 mg, 0.1 mmol) in CH_2Cl_2 (0.75 mL) was added **1** (0.43 g, 1.9 mmol), and the resultant reaction mixture was stirred at 25 °C. After complete conversion of **1** to [N=PCl_2]$_n$, as determined by ^{31}P NMR spectroscopic analysis (for [N=PCl_2]$_n$, ^{31}P-NMR (CH_2Cl_2): δ = −16.9), a portion of the polymerization mixture was treated with $NaOCH_2CF_3$ to produce the trifluoroethoxy derivative [N=P(OCH_2CF_3)$_2$]$_n$ (**2**).

GPC for **2**: $M_n = 2.0 \times 10^4$ and PDI = 1.01.

To the remainder of the reaction solution was added $PhF_2P=NSiMe_3$ (**7**) (0.8 g, 3.4 mmol) and the resultant mixture was stirred for 24 h with occasional monitoring by ^{31}P NMR spectroscopy. After complete conversion of **7** to polymer, as determined by ^{31}P NMR spectroscopy, all volatiles were removed at reduced pressure, and treatment of the resultant species {[N=PCl_2]$_x$[N=PF(Ph)]$_y$} **(12)** with $NaOCH_2CF_3$ produced {[N=P(OCH_2CF_3)$_2$]$_x$[N=PPh(OCH_2CF_3)]$_y$} (**10**), thus permitting molecular weight determination by GPC.

GPC for **10**: $M_n = 4.5 \times 10^4$ and PDI = 1.30. ^{31}P-NMR (CH_2Cl_2): δ = 3.1 (s, [N=PPh(OCH_2CF_3)]$_m$), −6.9 ppm (s, [N=P(OCH_2CF_3)$_2$]$_n$).

Macromolecular Substitution Reactions of [N=PF(Ph)]$_n$ with Metalloorganic Reagents. (a) Samples of **7** (0.44 g, 1.9 mmol) were treated with PCl_5 (0.02 g, 0.1 mmol) under solvent-free conditions with stirring at 35 °C. After 30 min the reaction mixture becomes immobile. All volatile species were removed at reduced pressure. Portions of the [N=PF(Ph)]$_n$ samples were removed (ca. 10%), dissolved in 10 mL of dioxane, and treated with 2.5 M sodium trifluoroethoxide (10 mmol) in dioxane (4 mL). These mixture were then refluxed for 48 h to produce the known macromolecule [N=P(Ph)(OCH_2CF_3)]$_n$ (**4**).

For **4**: (i) GPC: $M_n = 1.2 \times 10^4$, and PDI = 1.08; (ii) GPC, $M_n = 1.2 \times 10^4$, and PDI = 1.08; (iii) GPC, $M_n = 1.2 \times 10^4$, and PDI = 1.08.

The remaining portions of [N=PF(Ph)]$_n$ were dissolved in 25 mL of THF, cooled to −78 °C, and treated with stoichiometric amounts of (i) 1.4 M MeLi (1.2 mL, 1.7 mmol), ii) 1.6 M *n*-BuLi (1.0 mL 1.7 mmol), and (iii) 1.0 M *p*-tolylmagnesium bromide (1.7 mL, 1.7 mmol). After 45 min all volatiles were removed, and the resultant products were washed with hexanes (10 mL) and water (10 mL).

(i) [N=PPh(Me)]$_n$ (**13**). GPC: $M_n = 5.4 \times 10^3$ and PDI = 1.02. ^{31}P-NMR (CH_2Cl_2): δ = 0.2 ppm.[26]

(ii) [N=PPh(Bu)]$_n$ (**14**). GPC: $M_n = 5.6 \times 10^3$ and PDI = 1.12. ^{31}P-NMR (CH_2Cl_2): δ = 10.0 ppm.

(iii) [N=PPh(tolyl)]$_n$ (**15**). GPC: $M_n = 5.5 \times 10^3$ and PDI = 1.01. ^{31}P-NMR (CH_2Cl_2): δ = 5.1 ppm.[27]

(b) A sample of **7** (0.89 g, 3.8 mmol) was treated with PCl_5 (0.02 g, 0.1 mmol) in a 40:1 ratio under solvent free conditions, at 35 °C to produce [N=PF(Ph)]$_n$. All volatiles were removed at reduced pressure. Portions of the [N=PF(Ph)]$_n$ samples were removed (ca. 10%) and dissolved in 10 mL of dioxane and treated with 2.5 M sodium trifluoroethoxide (10 mmol) in dioxane (4 mL). The mixture was then refluxed for 48 h to produce the known macromolecule [N=P(Ph)(OCH_2CF_3)]$_n$ (**4**). ^{31}P-NMR (CH_2Cl_2): δ = 3.1 ppm.[27] GPC: $M_n = 5.5 \times 10^4$ and PDI = 1.26.

The remaining portion of [N=PF(Ph)]$_n$ was dissolved in 25 mL of THF, cooled to −78 °C, and treated with 1.4 M MeLi: (i) 1.2 mL (1.7 mmol) and (ii) 2.0 mL (2.85 mmol). After 45 min a solution of 2.5 M sodium trifluoroethoxide (10 mmol) in dioxane (4 mL) was added, and the reaction mixture was refluxed for 24 h. All volatiles were removed and the resultant products were washed with hexanes (100 mL) and water (150 mL).

(i) [[N=PPh(OCH_2CF_3)$_{0.5}$(Me)$_{0.5}$] (**16**). GPC: $M_n = 2.4 \times 10^4$ and PDI = 1.10. ^{31}P-NMR (CH_2Cl_2): δ = 2.3 ppm.[26] ^1H-NMR ($CDCl_3$): δ = 8.1−7.1 (br m, 5H, Ph), 4.3−3.5 (br, 1H, OCH_2-CF_3), and 1.6−1.2 ppm (br, m of d, 1.5H, $-CH_3$); ^{13}C-NMR ($CDCl_3$): δ = 136.2−131.3 (q, $^2J_{CF}$ = 45 Hz, $-CF_3$), 132.3−127 (br m, Ph), 62.2−61.0 (br q, $^3J_{CF}$ = 11, O−CH_2−) and 30.5−29.6 ppm (br, m of d, P−CH_3).

(ii) [[N=PPh(OCH_2CF_3)$_{0.25}$(Me)$_{0.75}$] (**17**): GPC: $M_n = 2.3 \times 10^4$ and PDI = 1.04: ^{31}P-NMR (CH_2Cl_2): δ = 2.2 ppm.[26] ^1H-NMR ($CDCl_3$): δ = 8.1−7.1 (br m, 5H, Ph), 4.3−3.5 (br, 0.5H, OCH_2CF_3), and 1.6−1.2 ppm (br, m of d, 2H, $-CH_3$).

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