Synthesis and Properties of High Polymeric Phosphazenes with (Trimethylsilyl)methyl Side Groups[1]

Harry R. Allcock* and William D. Coggio

Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802

Received March 30, 1992; Revised Manuscript Received September 30, 1992

ABSTRACT: Poly(organophosphazenes) that bear Me_3SiCH_2 side groups were prepared via the reaction of [(trimethylsilyl)methyl]lithium with poly(phenylfluorophosphazene) ($[NP(Ph)F(NPF_2)_2]_n$). Fluorine replacement occurred under mild conditions to yield polymers that contained up to 70% of the side groups as alkylsilyl units. Subsequent reaction with CF_3CH_2ONa gave air- and moisture-stable polymers with the basic stoichiometry of $[NP(Ph)_{0.34}(OCH_2CF_3)_{1.66-x}(CH_2SiMe_3)_x]_n$. The polymers were analyzed by ^{31}P, ^{1}H, and ^{19}F NMR spectroscopy, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). Replacement of the fluorine atoms by Me_3SiCH_2 side groups was accompanied by some skeletal cleavage. However, high molecular weight polymers were obtained by limiting the reaction time and temperature. Evidence was obtained that the organosilicon side groups are the sites of cross-linking reactions when the polymers are heated at temperatures above 200 °C.

A growing interest exists in the synthesis and properties of new macromolecules that contain main-group inorganic elements such as phosphorus, nitrogen, and silicon. Polymers such as poly(organosiloxanes), polysilanes, polysilazanes, and poly(organophosphazenes)[2-12] are the focus of considerable current research effort. Much of this effort is directed toward the development of new elastomers, fibers, biomedical materials, lithography coatings, and ceramics.[12-16]

In a series of recent papers[2-11] we have described several new classes of polymers that possess a phosphazene backbone and organosilicon side groups. These polymers may be viewed as molecular hybrids of polyphosphazenes and polysiloxanes or polysilanes, with molecular and materials properties that are some combination of the phosphorus and silicon based polymer systems. For example, a valuable feature of polyphosphazenes is the ease with which properties can be fine-tuned by facile variations in the side groups linked to the phosphorus atoms. Thus, properties such as solubility, crystallinity, and materials flexibility can be controlled easily. The presence of organosilicon side groups offers the prospect of hydrophobic surface character, biomedical compatibility, and possibly enhanced thermooxidative stability. The possibility also exists that the presence of silicon in the side group structure may provide a means for the preparation of cross-linked matrices that contain phosphorus, nitrogen, and silicon in ceramic-type structures.[15,16]

The previously known examples of hybrid organophosphazene–organosilicon polymers fall into the following categories.

(1) *Polymers Prepared by the Ring-Opening Polymerization of Cyclic Phosphazenes That Bear both Halogen and Organosilicon Side Groups.* This route requires that the halogen side units in the intermediate polymer must be replaced by reaction with an alkoxide or aryloxide nucleophile. For example, Allcock, Brennan, and Graaskamp[4,6] synthesized cosubstituent phosphazene polymers with both alkylsilyl and trifluoroethoxy side units via the ring-opening polymerization of *gem*-$N_3P_3(CH_2SiMe_3)_2Cl_4$ followed by further reaction with sodium trifluoroethoxide. A drawback of this approach is that a maximum of only two alkylsilyl side groups can be introduced per three P–N repeating units (only 33% of all side groups). Moreover, the macromolecular substitution step (for example, the reaction with sodium trifluoroethoxide) can lead to cleavage of organosilicon units from the chain unless special precautions are taken. Thus, limits exist to the percentage loading of organosilicon units in polymers prepared by this route.

(2) *Polymers Prepared by Metalation of Alkylphosphazene Polymers Followed by Reaction with Organosilicon Halides.* Neilson, Wisian-Neilson, and co-workers[17,18] have synthesized organosilicon–phosphazene polymers via the deprotonation of poly(methylphenylphosphazene) by *n*-BuLi, followed by reaction with a chloroorganosilane. The maximum of organosilicon groups along the polyphosphazene chain was reported to be about 50%.

(3) *Polymers Prepared by the Reactions of Organosilicon Chlorides with (Lithioaryloxy)phosphazene Polymers.* This method is similar to the one reported in (2) except that the para position of an aryloxy side group is the locus of metal–halogen exchange, with the lithioaryloxy derivative then being the site for coupling to an organosilicon halide or ring opening of a cyclosiloxane.[8] Polymers with up to 75% of the side groups bearing organosilicon units were prepared.

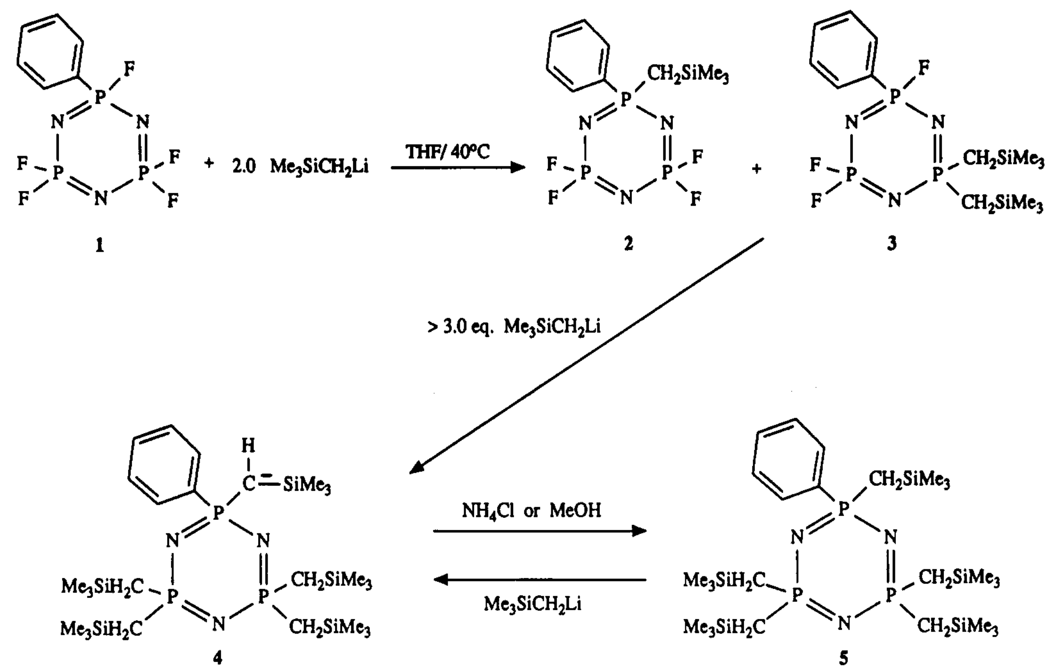
(4) *Reactions of Chlorophosphazene High Polymers with Aminosiloxane Reagents.* Depending on the reaction conditions, phosphazene polymers in which 100% of the side groups are aminoalkyl linear-siloxane units can be prepared by this method.[9] The only known drawback to these polymers is the relatively high cost of the (aminoalkyl)siloxane reagents. Nevertheless, this is a highly attractive route to new elastomers and materials with tailored surface properties.

(5) *Use of Hydrosilylation Reactions for the Coupling of Organic or Organometallic Side Groups to (Aminosiloxy)phosphazene Polymers.* This approach builds on the chemistry used in method 4 but adds the option that the organosilicon side units themselves become the sites for linkage to interesting and potentially useful tertiary structures such as vinylsiloxanes, epoxy cross-linking units, etc.[11]

In this paper we describe a sixth approach which involves the reactions of (organosilyl)lithium reagents with poly(*fluoro*phosphazenes). The logic behind this approach is as follows. An intuitively simple method for the synthesis of organosilicon-substituted polyphosphazenes is via the reactions of metallo-organosilicon derivatives with poly(dihalogenophosphazenes) such as poly(dichlorophosphazene). However, detailed earlier work in our program

0024-9297/93/2226-0764$04.00/0

Scheme I[a]



[a] The regiochemistry shown for the metal-hydrogen exchange reaction for 4 is an example only. The deprotonation is not specific to any particular Me_3SiCH_2 side group.

revealed that most organometallic reagents react with poly(dichlorophosphazene) not only to replace the halogen atoms but also to cleave the phosphorus-nitrogen backbone bonds.[19-22] The skeletal cleavage process can, however, be retarded by the use of poly(di*fluoro*phosphazene) as a macromolecular intermediate.[23] Moreover, as we reported recently, the cyclic trimer $(NPF_2)_3$ reacts with Me_3SiCH_2Li to give complete fluorine replacement without ring cleavage.[10] Thus, it seemed possible that fully or highly silylated polyphosphazenes might be accessible via the reactions between Me_3SiCH_2Li and fluorophosphazene high polymers. The only problem to extending the reaction of $(NPF_2)_3$ to the high-polymer level was the insolubility of high polymeric $(NPF_2)_n$ in all the normal solvents appropriate for organometallic chemistry.[23] However, poly(phenylfluorophosphazene) is soluble in common organic solvents, and so this polymer was employed in place of poly(difluorophosphazene).

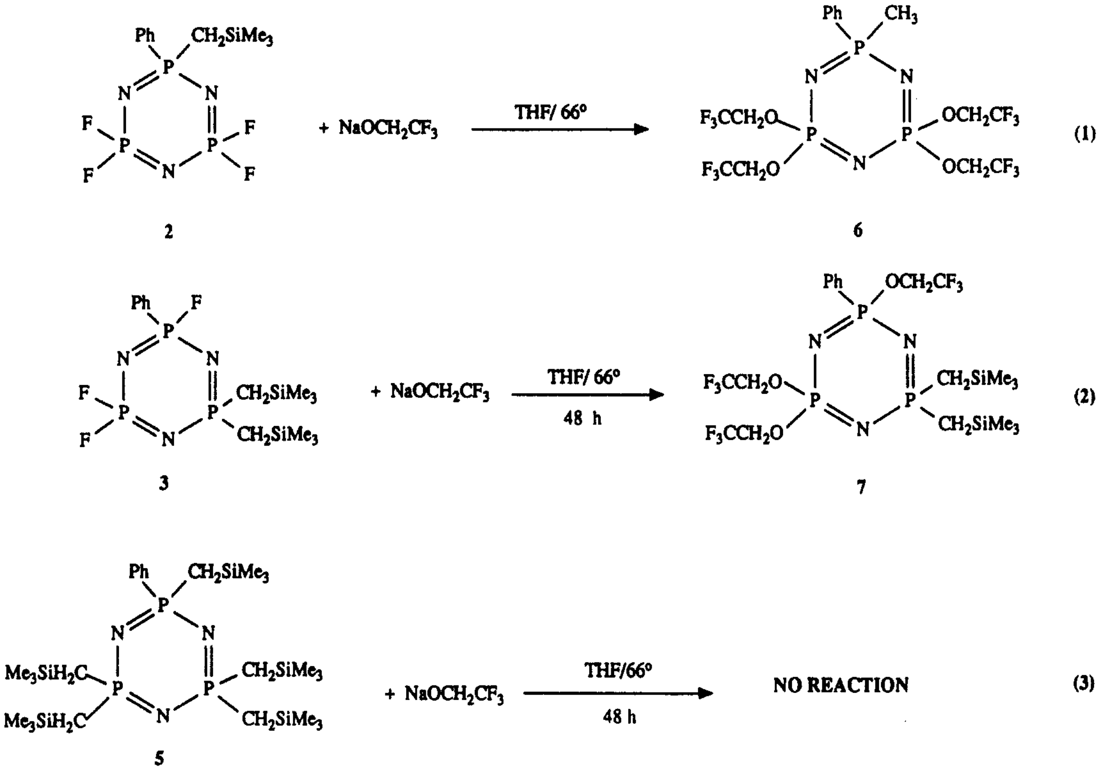
Several questions were kept in mind throughout this investigation. (1) Does Me_3SiCH_2Li react with $[NP(Ph)F(NPF_2)_2]_n$ without causing significant phosphorus-nitrogen bond cleavage? (2) If backbone cleavage does take place, at what stage in the substitution process does it occur? (3) Can Me_3SiCH_2 side groups be incorporated into the polymer together with cosubstituents such as trifluoroethoxy (CF_3CH_2O) or phenoxy (PhO)? (4) What is the behavior of these polymers at elevated temperatures under conditions that might lead to cross-linking and ultrastructure formation?

Results and Discussion

Model Reactions. (a) Replacement of Fluorine by Me_3SiCH_2 Groups. Although the reactions of $(NPF_2)_3$ with Me_3SiCH_2Li have been studied, no information existed about the reactions of $N_3P_3F_5Ph$ (1) with the same reagent. In particular, it was necessary to determine if the phenyl group in 1 might sterically retard the replacement of the geminal fluorine atom by Me_3SiCH_2. Thus the model reaction between Me_3SiCH_2Li and $N_3P_3F_5Ph$ was studied.

The replacement of the fluorine atoms in 1 by Me_3SiCH_2 groups was monitored by ^{31}P NMR spectroscopy and gas chromatography/mass spectrometry (GC/MS). The reaction was found to proceed rapidly in THF at 40 °C. As shown in Scheme I, the addition of 2.0 equiv of Me_3SiCH_2Li to a THF solution of 1 yielded a mixture of products. The compounds were identified by GC/MS as *gem*-$N_3P_3F_4Ph(CH_2SiMe_3)$ (2) and *gem*-$N_3P_3F_3Ph(CH_2SiMe_3)_2$ (3). Integration of the peak areas suggested that the reaction mixture consisted of 2 (15%) and 3 (85%). Further reaction of this mixture with excess Me_3SiCH_2Li gave the fully substituted product $N_3P_3Ph(CH_2SiMe_3)_5$ (5) in high yield. However, the formation of a complex intermediate, shown as 4 in Scheme I, was detected in the reaction mixture by ^{31}P NMR spectroscopy. This complex was identified by a series of broad peaks in the ^{31}P NMR spectrum between 34 and 26 ppm. Intermediate 4 is formed via a competing metal-hydrogen exchange reaction. The yield of 5 was maximized by the addition of a proton source, such as methanol or NH_4Cl, to the reaction mixture (see Scheme I). The details of this metal-hydrogen exchange reaction have been discussed in previous publications.[10,17-19] The high-yield synthesis of 5 provided support for the expectation that the phenyl group in 1 would not limit substitution of the fluorine atoms in the high polymer.

(b) C-Si Bond Cleavage Studies. Compounds 2 and 3 are models for the replacement of fluorine by trifluoroethoxy groups. In earlier work Allcock, Brennan, Graaskamp, and Dunn[3,4,6] described the base-catalyzed cleavage of the C-Si bonds in compounds such as $[NP(CH_2SiMe_3)_2(NPCl_2)_2]_n$ by CF_3CH_2ONa to generate phosphazenes which contained $P-CH_3$ units in place of $P-CH_2SiMe_3$ groups. This cleavage process is retarded by steric effects.[10] Thus, we were concerned that the macromolecules formed from 2 or 3 may undergo C-Si bond cleavage in the presence of CF_3CH_2ONa to produce polymers with methyl groups in place of alkylsilyl side groups.



Scheme II

It was found that **2** reacted with excess CF_3CH_2ONa in THF to undergo fluorine replacement by trifluoroethoxy side groups and that this reaction was accompanied by C–Si bond cleavage to produce *gem*-$N_3P_3(OCH_2CF_3)_4Ph(CH_3)$ (**6**) (see Scheme II, reaction 1). However, compound **3** reacted with excess CF_3CH_2ONa under the same conditions to give $N_3P_3(OCH_2CF_3)_3Ph(CH_2SiMe_3)_2$ (**7**) in high yield. No C–Si bond cleavage products were detected by either GC/MS or ^{31}P NMR analysis (Scheme II, reaction 2). Similarly, no reaction took place when **5** was exposed to excess CF_3CH_2ONa in THF at 66 °C for 48 h (Scheme II, reaction 3). Characterization data are listed in the Experimental Section.

These results indicate that, although C–Si bond cleavage is possible with relatively unhindered species (Scheme II, reaction 1), compounds that have intermediate steric crowding (i.e., **3**) undergo fluorine atom replacement by CF_3CH_2O in preference to C–Si bond cleavage. This provided encouragement for the view that, at the high-polymer level, replacement of fluorine by trifluoroethoxy may be possible without serious side reactions that involve the organosilicon groups.

Macromolecular Reactions between $[NP(Ph)F(NPF_2)_2]_n$ and Me_3SiCH_2Li. The reactions between **8** and Me_3SiCH_2Li are shown in Scheme III. As in the small-molecule model reactons, fluorine atom replacement occurred rapidly at 40 °C in THF. However, in contrast to the small-molecule reactions, complete replacement of the fluorine atoms by Me_3SiCH_2 groups did not occur under these conditions. Two factors appear to limit the extent of the organometallic substitution reaction. First, when fluorine replacement reaches a certain stage, the polymer precipitates from the reaction medium, and this essentially terminates the reaction. This behavior is ascribed to metal–hydrogen exchange reactions, similar to those identified in the cyclic trimer model systems. This side reaction would lead to a buildup of anionic charge on the polymer, with a resultant decrease in solubility. Second, the steric hindrance associated with the polymer chain may slow the rate of fluorine replacement, especially after each phosphorus atom bears one organosilicon side group.

The presence of residual P–F bonds could sensitize the polymers to hydrolysis and cross-linking. Hence, they were not isolated but were used as reactive intermediates for alternative halogen-replacement reactions.[12,13] Thus, these polymers were treated with CF_3CH_2ONa in the presence of a 100% excess of CF_3CH_2OH. The free alcohol protonated any methylene groups that had undergone metal–hydrogen exchange. After this step, the polymers redissolved, and this suggested that the initial insolubility was not due to cross-linking.[24]

Attempts were also made to replace the remaining fluorine atoms by phenoxy side groups. However, complete replacement of the fluorine atoms did not occur in THF at 66 °C, as determined by ^{19}F NMR spectroscopy. This result is attributed to the steric restrictions experienced by the bulky phenoxy anions.

Polymer Characterization. A series of polymers with different ratios of alkylsilyl to trifluoroethoxy side groups was prepared (see Scheme III) to study the effect of the Me_3SiCH_2 side groups on the polymer properties. The polymers were purified by sequential precipitations from concentrated THF solutions into water and hexane followed by Soxhlet extraction with hexane for 24 h. The polymers (**9a–e**) were isolated as light brown, air- and moisture-stable materials.

Characterization data for **9a–e** were obtained by ^1H, ^{19}F, and ^{31}P NMR spectroscopy. Proton and phosphorus NMR signals were broadened significantly because of solution viscosity effects. Polymers **9a–e** were found to have the basic stoichiometry of $[NP(Ph)_{0.34}(CH_2SiMe_3)_x(OCH_2CF_3)_{1.66-x}]_n$, with the value of x being deduced by ^1H NMR spectroscopy. The side group ratios were estimated by comparing the area of the $SiMe_3$ resonance at 0.1 ppm to the CF_3CH_2O resonance at 4.2 ppm.[25] Characterization data are listed in Table I.

The ^{31}P NMR spectra of **9b–e** showed three major types of broad featureless resonances, assigned to $P(Ph)(CH_2$-

Scheme III

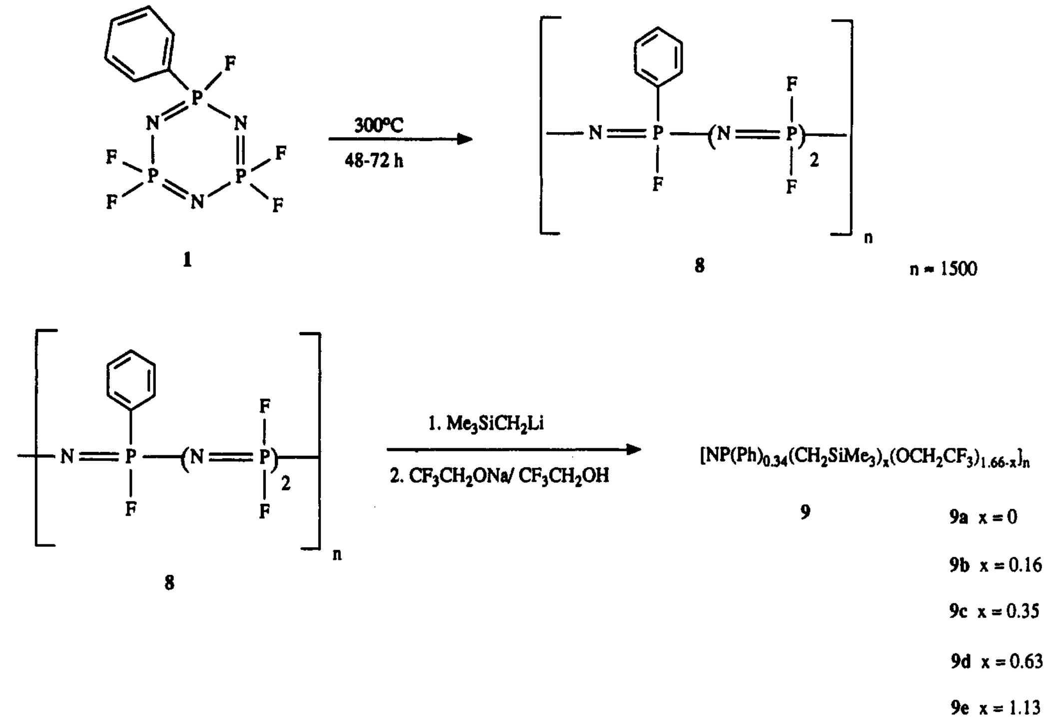


Table I
Analytical Data for Polymers

			^{31}P NMR[a]		^{1}H NMR		
compd	T_g (°C)	M_n (×10^{-4})	signal	shift (ppm)	signal	shift (ppm)	ratio
$[NP(Ph)_{0.34}F_{1.66}]_n$ (8)			PF_2	-23.0			
			$PFPh$	7.0	Ph	7.3-6.8	
$[NP(Ph)_{0.34}(OCH_2CF_3)_{1.66}]_n$ (9a)	-33	20.0	$P(OCH_2CF_3)_2$	-8.1	OCH_2CF_3	4.1	2.0
			$P(OCH_2CF_3)Ph$	3.8	Ph	7.3-6.8	1.0
$[NP(Ph)_{0.34}(OCH_2CF_3)_{1.5}R_{0.16}]_n$ (9b)		15.0	$P(OCH_2CF_3)_2$	-8.0	OCH_2CF_3	4.1	2.1
			$PPhR$	12.5	Ph	7.3-6.8	1.2
			PRR'	3.1-2.1	$SiMe_3$	0.3	1.0
$[NP(Ph)_{0.34}(OCH_2CF_3)_{1.3}R_{0.35}]_n$ (9c)	51	13.5	$P(OCH_2CF_3)_2$	-8.0	OCH_2CF_3	4.1	1.5
			$PPhR$	12.5	Ph	7.3-6.8	1.0
			PRR'	3.1-2.1	$SiMe_3$	0.3	1.8
$[NP(Ph)_{0.34}(OCH_2CF_3)_{1.03}R_{0.63}]_n$ (9d)	65	7.9	$P(OCH_2CF_3)_2$	-8.0	OCH_2CF_3	4.1	1.2
			$PPhR$	12.5	Ph	7.3-6.8	1.0
			PRR'	3.1-2.1	$SiMe_3$	0.3	3.4
$[NP(Ph)_{0.34}(OCH_2CF_3)_{0.53}R_{1.13}]_n$ (9e)	71	4.0	$P(OCH_2CF_3)_2$	-8.0	OCH_2CF_3	4.1	1.0
			$PPhR$	12.5	Ph	7.3-6.8	1.3
			PRR'	3.1-2.1	$SiMe_3$	0.3	7.0

[a] R = CH_2SiMe_3, R′ = CH_2SiMe_3 or OCH_2CF_3.

$SiMe_3$) (12.3 ppm), $P(CH_2SiMe_3)_2$, $P(OCH_2CF_3)(CH_2SiMe_3)$ (3.1–1.2 ppm), and $P(OCH_2CF_3)_2$ (−8.2 ppm) units. The ^{19}F NMR spectra contained a broad singlet at 38.4 ppm from the CF_3 groups, with no evidence for residual P–F bonds (54 ppm, J_{PF} = 800 Hz) in 9a–e. From these analyses it was concluded that the polymers were at least 95% substituted by either the Me_3SiCH_2 or the CF_3CH_2O side groups.

Thermal analyses of the polymers were obtained by differential scanning calorimetry. Polymer 9a has a T_g of −33 °C. Polymers 9b–e were amorphous, rigid materials with T_g's between +51 (9c) and +73 °C (9e), depending on the loading of CH_2SiMe_3 units.[26] Infrared analysis showed bands consistent with the assigned structures[27] (see Table I for further details).

Attempts To Bring about Complete Substitution. Several experiments were carried out to determine the upper limit for the replacement of fluorine atoms by the alkylsilyl side groups. Analyses of reaction mixtures in which THF solutions of Me_3SiCH_2Li alone were added to a THF solution of 8 suggested that a maximum of approximately 70% of the fluorine atoms could be replaced. Surprisingly, despite the presence of unreacted P–F bonds, these polymers were sufficiently stable to atmospheric moisture to allow purification and subsequent analysis by NMR spectroscopy. However, extended exposure to the atmosphere caused these materials to become insoluble, presumably because of P–F bond hydrolysis and subsequent cross-linking. The ^{19}F NMR spectra of these species showed two broad resonances, which were consistent with the presence of residual P–F bonds. When 8 was added to a large excess (~150%) of Me_3SiCH_2Li under refluxing conditions for 12 h, full replacement of the fluorine atoms apparently occurred.[28] However, GPC analysis showed that the polymer molecular weight had declined to M_n < 16 000.

Molecular Weight Decline during Substitution. It was important to establish the degree to which the (organosilyl)lithium reagent attacked the polymer backbone during the initial fluorine replacement process. Thus, different samples of polymer 8 were treated with different amounts of Me_3SiCH_2Li. The remaining fluorine atoms

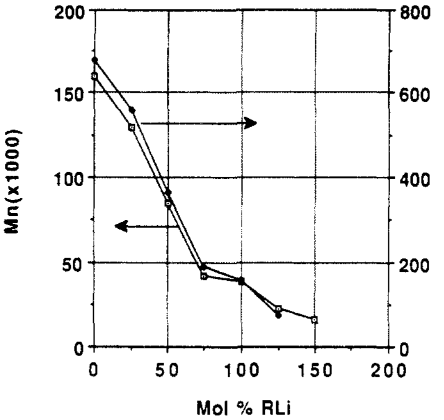


Figure 1. Relationship between GPC-average molecular weight (similar to M_n) and the mole percent of Me_3SiCH_2Li used for preparation of polymers **9a–e**. The related curve for the variation in repeating units provides a correction to take into account the change in side group structure as substitution occurs. GPC samples were prepared at a concentration of 2% bulk weight in THF.

Table II
Weight Loss for Polymers Heated First at 200 °C and Then to 900 °C[a]

compd	% Me_3SiCH_2	% wt loss at 200 °C	tot % wt loss at 900 °C	onset (°C)
$[NP(OCH_2CF_3)_2]_n$	0	4.0	97	466
$[NP(CH_3)_2]_n$	0	14.2	99	532
9a	0	<1.0	90	460
9b	10	2.6	73	430
9c	21	3.2	69	413
9d	38	4.0	58	424
9e	62	4.0	49	377

[a] The isothermal heating at 200 °C was for 2.5 h, followed by a temperature rise at a rate of 10 °C/min, all under a nitrogen atmosphere.

were then replaced by trifluoroethoxy groups, and the products were analyzed by GPC. In these experiments, five polymers that contained 0, 21, 38, 62, and ~100% of Me_3SiCH_2 side group were used. A relationship between the GPC-average molecular weight (approximating to M_n) and the mole percent Me_3SiCH_2Li used in the substitution is shown in Figure 1. It was found that some molecular weight decline did occur as larger amounts of Me_3SiCH_2Li were used. However, as fluorine atoms were replaced by Me_3SiCH_2 groups, the polymer chains became resistant to further degradation, and the amount by which the molecular weight declined became less. This trend is illustrated by the change of the slope in Figure 1. For example, the molecular weight decline from polymer **9c** (50% Me_3SiCH_2Li used) to **9d** (75% Me_3SiCH_2Li used) was ~50%, whereas the decline from **9d** to **9e** (100% Me_3SiCH_2Li used) was only ~20%. The decrease in the extent of chain cleavage at higher loadings of the Me_3SiCH_2 side group probably reflects the steric effect of the bulky alkylsilyl groups which protects the polymer backbone from further degradation.

Pyrolysis of $[NP(Ph)_{0.34}(CH_2SiMe_3)_x(OCH_2CF_3)_{1.66-x}]_n$. Polymers **9a–e** were analyzed by thermogravimetric analysis (TGA). For comparison purposes, pyrolysis data for $[NP(OCH_2CF_3)_2]_n$ and $[NPMe_2]_n$ were also obtained. These results are shown in Figure 2 and are listed in Table II.

It is apparent from Figure 2 that, as the loading of Me_3SiCH_2 units in the polymer increases, the amount of volatile material released decreases. For example, polymer **9a** (0% Me_3SiCH_2) was found to retain only 10% of its weight after being heated to 900 °C. However, with a 10% incorporation of alkylsilyl side groups (**9b**), the weight retention of the polymer increased to 27%. This trend of higher weight retention with higher incorporation of Me_3SiCH_2 units continued for the other polymers in the series (see Table II).

The residues from the pyrolyses were glassy, graphite-like materials. Infrared spectra of the residues in KBr pellets showed only broad absorptions at 1030, 1100, and 1280 cm^{-1}. A solid-state ^{13}C NMR spectrum consisted of a single broad resonance centered at 120 ppm, which was consistent with a graphite-like structure. No evidence for the presence of Si–C groups was found by solid-state ^{13}C NMR analysis. A solid-state ^{31}P NMR spectrum of the residue showed that at least two different types of phosphorus environments were present. Both signals were in the range of 12.0–4.0 ppm and were consistent with alkylphosphazene structures. No resonances associated with the presence of CF_3CH_2O groups were detected. It was apparent from these results that the Me_3SiCH_2 units in the polymers had the effect of increasing the gross thermal stability[29] and weight retention. Although the organosilicon-containing polymers **9b–e** underwent an initial weight loss at temperatures that were lower than for **9a**, $[NP(OCH_2CF_3)_2]_n$, or $[NPMe_2]_n$ (see Table II), these control samples volatilized completely at temperatures above 450–500 °C. An explanation for these differences is as follows.

First, the control polymers, $[NP(OCH_2CF_3)_2]_n$ and $[NPMe_2]_n$, are known to undergo thermally-induced depolymerization–equilibration reactions to produce small-molecule cyclic species.[30] This equilibration process is evident from the profile of the TGA curves in Figure 2 in which the abrupt weight loss probably reflects the volatalization of discrete small-molecule species such as the cyclic trimer. Thus, the control polymers **9a**, $[NPMe_2]_n$, and $[NP(OCH_2CF_3)_2]_n$ undergo a faster weight loss in the higher temperature regions than do polymers (**9b–e**) which possess alkylsilyl units. This suggests that the organosilicon side groups either participate in a cross-linking process or they restrict the ability of the chain to undergo the back-biting reactions that are necessary for the formation of small-molecule cyclic species.[31]

Strong evidence was obtained that the organosilicon units are the locus of a cross-linking reaction. First, the TGA curves for **9b–e** show a steady weight loss over a broad temperature range. Such a profile is consistent with a reaction which involves the gradual loss of low molecular weight products from the side groups rather than a loss of small-molecule cyclic species formed by skeletal cleavage. This process is outlined schematically in Scheme IV.

Second, TGA/MS analysis allowed the products of thermolysis to be identified as each reaction proceeded. Polymers **9b–e** were studied by this technique, as well as the non-silicon-containing control species. As shown in Figure 2, each pyrolysis procedure consisted of a 2.5-h isotherm at 200 °C, followed by temperature increases to 900 °C. A small percentage of weight loss occurred at 200 °C (see Table II). However, the weight loss at 200 °C increased as the percentage of the Me_3SiCH_2 units in the polymer increased.

As a specific example, the mass spectrum of **9c** was obtained as the sample probe was heated at 200 °C. Fragments detected from the polymer included $SiMe_3$ and CH_3 units; however, no phosphazene cyclic species were detected. This suggested that units such as PCH_2 or PCH_2SiMe_2 remained bonded to the polymer. We speculate that these units participate in the cross-linking reactions at elevated temperatures. Indeed, a sample of **9c** became

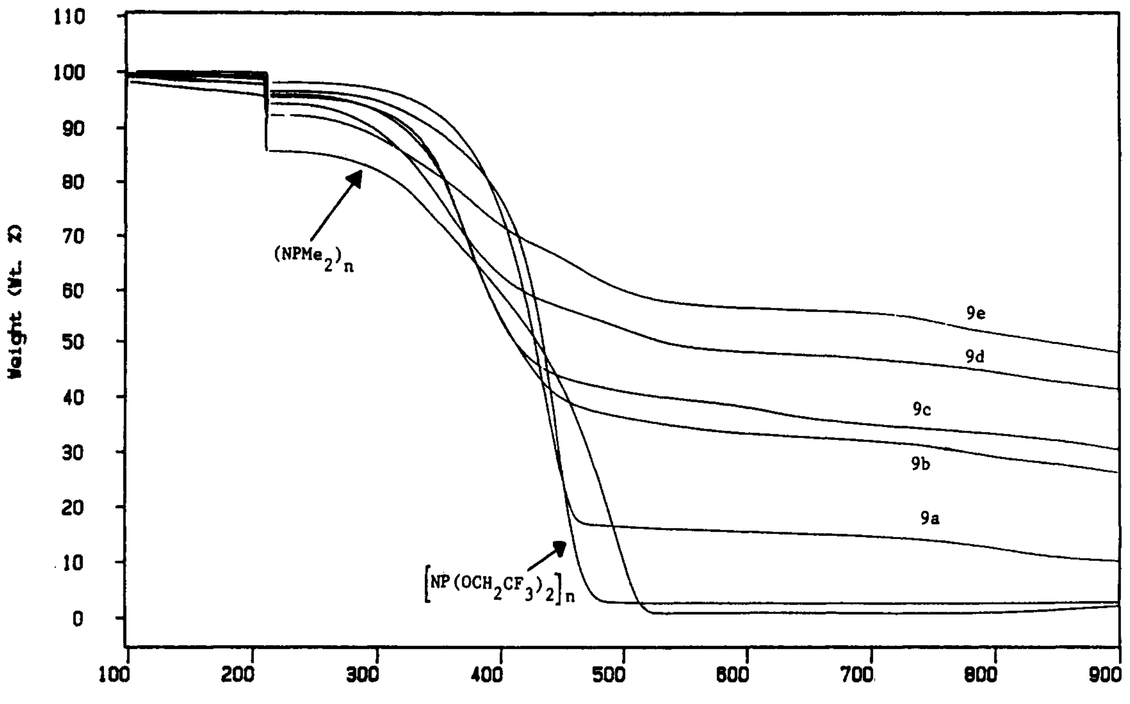
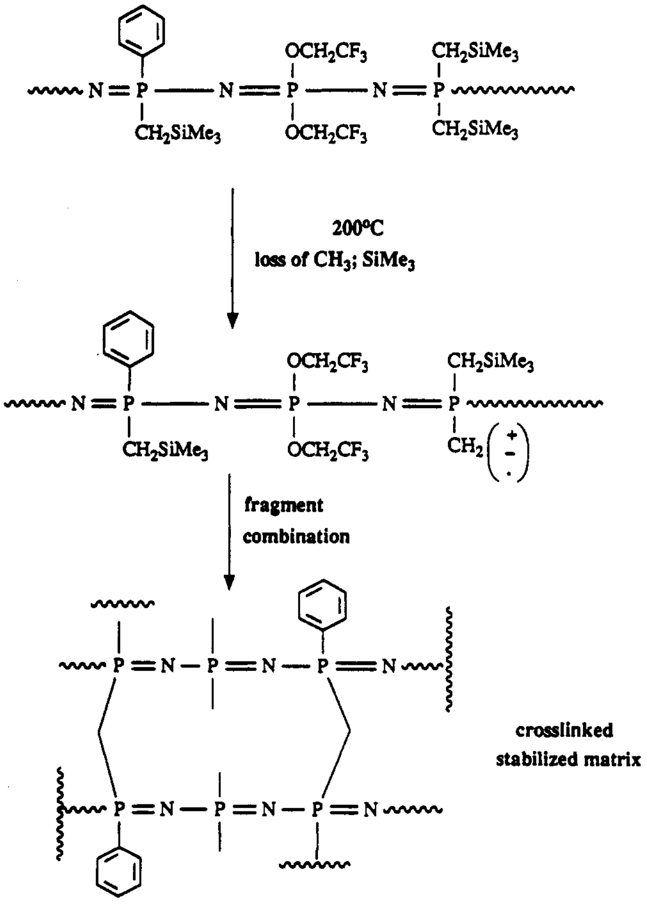


Figure 2. TGA thermograms of polymers **9a–e**, [NPMe$_2$]$_n$, and [NP(OCH$_2$CF$_3$)$_2$]$_n$. The samples were heated isothermally at 200 °C for 2.5 h and were then heated at a rate of 10 °C/min to 900 °C under an atmosphere of nitrogen.

Scheme IV



insoluble when heated in air at 200 °C for 6 h. Trifluoroethoxy, phenyl, and higher molecular weight fragments (>600 amu) were detected in the mass spectrum of **9c**, but only at higher temperatures (350 °C). However, by the time these temperatures were reached, substantial cross-linking of linear or cyclic fragments had already occurred. By contrast, the weight loss at 200 °C experienced by [NPMe$_2$]$_n$ was significantly more than found for **9a–e**, and this weight loss was apparently due to vaporization of cyclic species formed by thermally-induced equilibration processes.[30] Thus, the polymers that contained the Me$_3$SiCH$_2$ side group formed cross-linked networks in preference to equilibration–depolymerization products at temperatures near 200 °C. The final products of pyrolysis at 900 °C contained mainly carbon, phosphorus, and nitrogen.

Experimental Section

Equipment. ^{31}P (36.2 MHz), ^{19}F (84.3 MHz), and ^{13}C (22.5 MHz) NMR spectra were obtained with a JEOL FX 90Q spectrometer; references were relative to external 85% H$_3$PO$_4$, C$_6$H$_5$F, and SiMe$_4$, respectively. High-field ^{31}P NMR (120.5 MHz) and ^{1}H NMR (300.3 MHz) spectra were obtained with a Bruker AM 300 spectrometer. All heteronuclear NMR spectra were proton decoupled unless otherwise specified. Solid-state ^{13}C and ^{31}P spectra employed the magic angle spinning (MAS) technique.[33] Cross polarization was not used for the solid-state ^{13}C NMR spectra because of the lack of hydrogen in the materials. Spectra were obtained by use of a Chem-Magnetics 300 solid-state NMR spectrometer operating at fields of 75.0 and 120.5 MHz, respectively. Infrared spectra were recorded by use of a Perkin-Elmer 1710 FTIR interfaced with a Perkin-Elmer 3600 Data Station. Differential scanning calorimetry (DSC, Perkin-Elmer Thermal Analysis System 7) was used to obtain glass transition temperatures. DSC samples were heated to 150 °C and were rapidly quenched to −100 °C. Data were collected at a heating rate of 10 °C/min. Sample sizes were between 5 and 10 mg. Thermogravimetric analysis (TGA) data were obtained by use of a Perkin-Elmer TGA-7 or a DuPont thermal analysis system. TGA experiments were carried out with the samples heated at a rate of 10 °C/min in an atmosphere of N$_2$ unless otherwise stated. Gel permeation chromatography was conducted by use of a Hewlett-Packard 1090 LC. The columns were calibrated against polystyrene standards. The molecular weights are considered to be approximate only. Solutions were prepared at a concentration of ~2% bulk weight in HPLC grade THF (Omnisolv). Samples were eluted with THF containing (n-Bu)$_4$N$^+$Br$^-$.

Hexachlorocyclotriphosphazene was kindly provided by Ethyl Corp. and was recrystallized from hexane and sublimed (30 °C, 0.05 mmHg) before use. Solvents were distilled from sodium benzophenone ketyl. 2,2,2-Trifluoroethanol (Halocarbon) was distilled from anhydrous BaO. All manipulations were conducted using standard Schlenk line techniques. Phenyllithium (1.4 M in diethyl ether) and [(trimethylsilyl)methyl]lithium (1.0 M in pentane) were obtained from Aldrich and were used as received.

Hexafluorocyclotriphosphazene and $N_3P_3F_5Ph$ (1) were prepared by procedures reported previously.[34,35] All reactions using Me_3SiCH_2Li were carried out with the use of dry glassware and solvents. Me_3SiCH_2Li (1 M solution in pentane) was stored at 10 °C and was allowed to warm to 25 °C before use to ensure a consistent concentration.

Synthesis of $N_3P_3(CH_2SiMe_3)_5Ph$ (5). Compound 1 was prepared by the method of Allen and Moeller[35] and was dried by distillation from CaH_2 to give material with bp 55–58 °C at 0.5 mmHg. To a reaction flask equipped with an addition funnel, condenser, and a stirrer bar were added 5.0 g (16.5 mmol) of 1 and dry THF (100 mL). The solution was warmed to ~40 °C. To this solution was added Me_3SiCH_2Li (90 mL, 5.5 equiv) in pentane over a 30-min period, during which time the reaction mixture turned light yellow. After ~2 h a ^{31}P NMR spectrum of the reaction mixture showed a complex series of peaks between 35 and 26 ppm. Methanol was added slowly to the NMR tube (*use caution!*). A ^{31}P NMR spectrum of this solution produced an AB_2 pattern with no evidence of PF coupling. Excess methanol was added slowly to the reaction mixture (*Caution*: a vigorous exotherm will result) and the mixture was stirred for 5 min. The pentane was removed under vacuum, and the remaining solution was poured into water and extracted twice with CH_2Cl_2. The organic layers were combined and dried over $MgSO_4$. Solvent removal produced a light yellow oil, which was purified by column chromatography on silica gel using hexane:CH_2Cl_2 (5:1). Isolated 7.3 g (72% yield).

Analytical data: ^{31}P NMR ($CDCl_3$, ppm) AB_2, $\delta_A = 25.2$ ($P(CH_2SiMe_3)_2$), $\delta_B = 16.8$ ($PPh(CH_2SiMe_3)$); $^2J_{PP}$ = unresolved. ^1H NMR ($CDCl_3$, ppm) 7.2–6.8 (m, phenyl), 1.23 (d, CH_2, $^2J_{PH} = 17.7$ Hz), 0.1 (s, $SiMe_3$). ^{13}C NMR ($CDCl_3$, ppm) 128–118 (phenyl), 27.5 (d, CH_2, $J_{PC} = 81$ Hz, $^3J_{PC} = 1.4$ Hz), 0.6 (s, $SiMe_3$). Mass spectral anal.: calcd, 647; found 647. Anal. Calcd for $C_{26}H_{60}N_3P_3Si_5$: C, 48.17; H, 9.35; N, 6.48. Found: C, 47.70; H, 9.20; N, 6.30.

Synthesis of *gem*-$N_3P_3Ph(CH_3)(OCH_2CF_3)_4$ (6). Compound 6 was formed in approximately 15% yield from a reaction in which 2.0 equiv of Me_3SiCH_2Li was added to $N_3P_3F_5Ph$ (1) in THF. The intermediate product, $N_3P_3F_4Ph(CH_2SiMe_3)$ (2), was identified by GC/MS analysis of the reaction mixture. Subsequent treatment of the product mixture containing 2 and 3 with CF_3CH_2ONa resulted in complete fluorine replacement together with C–Si bond cleavage of the Me_3SiCH_2 group in 2. Compound 6 was isolated from the reaction mixture by column chromatography (further details are provided below). Compound 6 has been synthesized previously by an alternative method.[5]

Analytical data: ^{31}P NMR ($CDCl_3$, ppm) AB_2, $\delta_A = 31.2$ (t, $P(Ph)CH_3$), $\delta_B = 15.2$ (d, $P(OCH_2CF_3)_2$); $^2J_{PP} = 32.9$ Hz. ^1H NMR ($CDCl_3$, ppm) 7.8–7.5 (m, phenyl), 1.74 (dt, CH_3, $^2J_{PH} = 14.6$ Hz, $^4J_{PH} = 2.0$ Hz). ^{13}C NMR ($CDCl_3$, ppm) 135–132 (phenyl), 22.0 (dt, CH_3, J_{PC} 126 Hz, $^3J_{PC} = 3.0$ Hz). Mass spectral anal.: calcd, 623; found, 623.

Synthesis of *gem*-$N_3P_3(OCH_2CF_3)_3Ph(CH_2SiMe_3)_2$ (7). To a reaction flask equipped with an addition funnel, condenser, and a stirrer bar were added 2.5 g (9.0 mmol) of 1 and dry THF (200 mL). To this solution was added Me_3SiCH_2Li (18.1 mL, 2.0 mmol) in pentane over a 30-min period during which time the reaction mixture turned light yellow. A ^{31}P NMR spectrum of the reaction mixture showed a complex series of peaks consistent with the structure *gem*-$N_3P_3F_3Ph(CH_2SiMe_3)_2$ (3). The reaction mixture was stirred at room temperature for 8 h to ensure complete formation of the product. A portion of this reaction mixture was saved for GC/MS analysis. It was concluded that 85% of the product was 3, and the remaining compound was identified as *gem*-$N_3P_3F_4Ph(CH_2SiMe_3)$ (2). To the reaction mixture containing 2 and 3 was added 6 equiv of CF_3CH_2ONa. The solution was stirred at 25 °C for 12 h and heated further for 6 h at 66 °C to ensure full substitution. The reaction was terminated when no further change was detected by ^{31}P NMR spectroscopy. The THF was removed under reduced pressure, and the resultant light yellow oil was chromatographed on a column packed with silica gel and hexanes. The compound was isolated by elution with 15% methylene chloride in hexanes.

Analytical data: ^{31}P NMR ($CDCl_3$, ppm) ABC, $\delta_A = 39.8$ ($P(CH_2SiMe_3)_2$), $\delta_B = 24.1$ ($PPh(OCH_2CF_3)$), $\delta_C = 11.6$ ($P(OCH_2CF_3)_2$); $^2J_{AB} = 7.3$ Hz, $^2J_{AC} = 24.8$ Hz, $^2J_{BC} = 38.1$ Hz. ^1H NMR ($CDCl_3$, ppm) 7.2–6.8 (m, phenyl), 4.2 (m, OCH_2CF_3), 1.23 (d, CH_2, $^2J_{PH} = 17.0$ Hz), 0.1 (s, $SiMe_3$). ^{13}C NMR ($CDCl_3$, ppm) 138–118 (phenyl, CF_3, $J_{CF} = 250$ Hz), 67.8 (q, OCH_2, $^2J_{CF} = 80.0$ Hz), 27.5 (d, CH_2, $J_{PC} = 81$ Hz, $^3J_{PC} = 1.4$ Hz), 0.6 (s, $SiMe_3$). Mass spectral anal.: calcd, 683; found, 683. Anal. Calcd for $C_{20}H_{33}F_9N_3O_3P_3Si_2$: C, 35.13; H, 4.88; N, 6.15. Found: C, 34.72; H, 4.54; N, 6.15.

Polymer Reactions. Thermal polymerization of 1 was achieved by heating 1 in a sealed, evacuated tube at 300 °C for 48–72 h.[36] The polymerization was terminated when the contents of the tube became light yellow and highly viscous. The tube was opened in a nitrogen-filled glove bag, and the entire contents (including glass) were transferred to a dry flask where the polymer was dissolved in dry THF. The polymer solution was filtered through a cotton plug under nitrogen into a clean, dried, weighed reaction flask. The solvent was removed, and the polymer was dried under vacuum for 24 h at 40 °C and then weighed. Typically, 2.5–3.0 g of polymer 8 was obtained by this procedure (yield >90%). See Table I for ^{31}P NMR analysis.

Polymer 8 was dissolved in dry THF (1.0 g/80 mL) and was warmed to ~40 °C. To this solution was added 6.5 equiv of Me_3SiCH_2Li (1 M solution in pentane). After approximately 20% of the lithium reagent had been added, the reaction became light yellow, and precipitated polymer adhered to the sides of the reaction flask. Vigorous stirring was employed until all the lithium reagent had been added. After approximately 30 min, the mixture was treated with 6.5 equiv of CF_3CH_2ONa and 6.5 equiv of CF_3CH_2OH in THF and was refluxed for 5 h. The polymer redissolved, and the solution was then concentrated and precipitated into water. The polymer was redissolved in THF and purified further by multiple reprecipitations from THF into water and hexanes. Full characterization data are listed in Table I.

Analysis of Molecular Weight vs Percent Me_3SiCH_2Li (9a–e). Polymer obtained from a single polymerization of 1 was used in this experiment to ensure that the initial molecular weight of polymer 8 was the same for all reactions. Thus 5.0 g (16.3 mmol) of 8 was dissolved in exactly 100 mL of dry THF to give a standard solution containing 0.05 g/mL of 8. From this solution four 15-mL portions (0.75 g, 12.2 mmol in terms of P–F bonds) were transferred to four separate reaction flasks equipped with a graduated addition funnel, a condenser, and a magnetic stirrer bar. The polymer solutions were then diluted with an appropriate amount of THF such that the final volume of each reaction was 100 mL. An appropriate amount of Me_3SiCH_2Li (1 M solution in pentane), calculated to replace either 0, 15, 25, 50, or 75% of the fluorine atoms in 8, was transferred to the addition funnels. Because of the competing metal–hydrogen exchange reaction, the actual incorporation of the Me_3SiCH_2 group was less than calculated. The polymer solutions were then warmed to 40 °C, and the Me_3SiCH_2Li was added. After 30 min the reaction mixtures were treated with CF_3CH_2ONa (15 mmol) containing CF_3CH_2OH (15 mmol) in THF and were stirred for 12 h at 60 °C. The polymers were purified by precipitations into water and hexanes, followed by Soxhlet extraction with methanol for 24 h. Characterization data are listed in Table I. GPC samples were prepared by dissolving 50 mg of polymer in 5 mL of THF.

Acknowledgment. We thank the Air Force Office of Scientific Research for financial support of this work. We also thank A. J. Benesi and R. Dudenhoefer for assistance with the solid-state NMR and TGA experiments, J. Blank and L. Collins for conducting the TGA/MS and GC/MS experiments, and C. J. Nelson for assisting with some of the experiments.

References and Notes

(1) This paper is the eleventh from our laboratory on organosilicon derivatives of phosphazenes. For previous papers in this series, see refs 2–11.

(2) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.

(3) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Organometallics* **1986**, *5*, 2434.

(4) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.

(5) Allcock, H. R.; Brennan, D. J.; Dunn, B. S.; Parvez, M. *Inorg. Chem.* **1988**, *27*, 3226.

(6) Allcock, H. R.; Brennan, D. J. *J. Organomet. Chem.* **1988**, *341*, 231.

(7) Allcock, H. R.; Brennan, D. J.; Dunn, B. S. *Macromolecules* **1989**, *22*, 1534.

(8) Allcock, H. R.; Coggio, W. D.; Archibald, R. S.; Brennan, D. J. *Macromolecules* **1989**, *22*, 3571.

(9) Allcock, H. R.; Coggio, W. D. *Macromolecules* **1990**, *23*, 1626.

(10) Allcock, H. R.; Coggio, W. D.; Parvez, M.; Turner, M. L. *Oraganometallics* **1991**, *10*, 677.

(11) Allcock, H. R.; Nelson, C. J.; Coggio, W. D. *Organometallics* **1991**, *10*, 3819.

(12) (a) Allcock, H. R. *Chem. Eng. News* **1985** (March 18), *63*, 22. (b) Zeldin, M.; Wynne, K. J.; Allcock, H. R., Eds. *Inorganic and Organometallic Polymers*; ACS Symp. Ser. 360; American Chemical Society: Washington, DC, 1987. (c) Mark, J. E.; Allcock, H. R.; West, R. C. *Inorganic Polymers*; Prentice-Hall: Englewood Cliffs, NJ, 1991.

(13) (a) *Phosphorus-Nitrogen Compounds*; Academic Press: New York, 1972. (b) Also see: Allcock, H. R. In *Comprehensive Polymer Science*; Pergamon Press: New York, 1989; Vol. 4, Chapter 26.

(14) Allcock, H. R.; Kwon, S.; Riding, G. H.; Fitzpatrick, R. J.; Bennett, J. L. *Biomaterials* **1988**, *9*, 509.

(15) See ref 13b, Chapters 3 and 11, and references therein.

(16) Wynne, K. J.; Rice, R. W. *Annu. Rev. Mater. Sci.* **1984**, *14*, 297.

(17) (a) Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910. (b) Allcock, H. R.; Allen, R. W.; O'Brien, J. P. *J. Am. Chem. Soc.* **1977**, *99*, 3984.

(18) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089. Also see: Neilson, R. H.; Wisian-Neilson, P. *Chem. Rev.* **1988**, *88*, 541.

(19) Allcock, H. R.; Desorcie, J. L.; Riding, G. H. *Polyhedron* **1987**, 6, 119.

(20) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolecules* **1981**, *14*, 218.

(21) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.

(22) Paddock, N. L.; Ranganathan, T. N.; Todd, S, M. *Can. J. Chem.* **1971**, *49*, 164. Also see: Paddock, N. L.; Ranganathan, T. N.; Todd, S. M. *Inorg. Chem.* **1973**, *12*, 316.

(23) The preparation of poly(difluorophosphazene) requires the use of a high-pressure autoclave. When formed, the polymer is soluble only in fluorinated solvents. See: Evans, T. L.; Allcock, H. R. *J. Macromol. Sci.* **1981**, *A16* (1), 409.

(24) This solubility behavior has been detected previously in other polyphosphazene systems known to contain anionic side groups. See ref 8 and Wisian-Neilson, P.; Islam, M. S. *Macromolecules* **1989**, *22*, 2026.

(25) Although an integration of the peaks in the ^{1}H NMR spectrum provided evidence for the stoichiometry of these polymers, their ceramic nature prevented the use of elemental analysis to corroborate the ^{1}H NMR data. Carbon, hydrogen, and nitrogen analyses were consistently low because of incomplete combustion. Such results for ceramic materials have been reported previously. See: Wu, H.; Interrante, L. V. *Chem. Mater.* **1989**, *1*, 564 and references therein.

(26) No T_g was detected for **9b** by DSC analysis. However, **9b** was more flexible than **9c–e** and may perhaps possess a T_g between those of **9a** and **9c**.

(27) Infrared spectral analysis gave absorption bands that were consistent with the presence of aryl, alkyl, Si–C, and P=N groups at 3030, 2950, 1260, and 1160 cm^{-1}, respectively.

(28) ^{19}F NMR spectroscopy of these species showed no signal even after 250 scans. Also the ^{31}P NMR spectra consisted of two featureless resonances at approximately 12.5 ppm for $P(Ph)(CH_2SiMe_3)$ and 3.0 ppm for $P(CH_2SiMe_3)_2$. However, the possibility exists that some P–F bonds remained in the polymer but were below the limits of detection by the NMR method.

(29) The term "thermal stability" is used in the context of the weight percent of the material that remains after pyrolysis to 900 °C. Studies conducted in our laboratory on the thermal behavior of polyphosphazenes suggest that weight loss onset temperatures, as determined by TGA, can lead to erroneous conclusions about the actual thermal stability of the polymers. See ref 30.

(30) Allcock, H. R.; McDonnell, G. S.; Riding, G. H.; Manners, I. *Chem. Mater.* **1990**, *2*, 425.

(31) Allcock, H. R.; Lampe, F. W. *Contemporary Polymer Chemistry*; Prentice-Hall: Englewood Cliffs, NJ, 1981; Chapter 7.

(32) Noll, W. *Chemistry and Technology of Silicones*; Academic Press: New York, 1968; Chapters 6, 7. Vornokov, M. *The Siloxane Bond*; Academic Press: New York, 1978; Chapters 3, 4.

(33) Fyfe, C. A. *Solid State NMR for Chemists*; C.F.C. Press: Ontario, 1983.

(34) Schmutzler, R. *Inorg. Synth.* **1967**, *9*, 75.

(35) Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2177.

(36) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.