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Ring-Opening Polymerization of Methylsilane- and Methylsiloxane-Substituted Cyclotriphosphazenes[1]

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ABSTRACT: The thermal polymerization behavior of cyclic trimeric phosphazenes that bear organosilylmethylene or organosiloxymethylene side groups, of general formula $N_3P_3Cl_5R$, *gem*-$N_3P_3Cl_4R_2$, and *gem*-$N_3P_3Cl_4(CH_3)R$, where R = CH_2SiMe_3, $CH_2SiMe_2OSiMe_3$, and $CH_2\overline{Si(Me)(OSiMe_2)_3O}$, has been studied. Species $N_3P_3Cl_5CH_2SiMe_3$, *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$, and *gem*-$N_3P_3Cl_4(CH_3)R$ undergo a phosphazene ring-opening polymerization to yield phosphazene high polymers that bear organosilicon side groups. However, those compounds of formula $N_3P_3Cl_5R$ and *gem*-$N_3P_3Cl_4R_2$ where R = $CH_2SiMe_2OSiMe_3$ and $CH_2\overline{Si(Me)(OSiMe_2)_3O}$ undergo thermally induced PCH_2–Si and Si–O bond cleavage reactions in preference to polymerization. The neopentyl derivative, $N_3P_3Cl_5CH_2CMe_3$, polymerized at 250 °C, but *gem*-$N_3P_3Cl_4(CH_3)(CH_2CMe_3)$ did not. However, both compounds copolymerized with their organosilicon counterpart, i.e., with $N_3P_3Cl_5CH_2SiMe_3$ and *gem*-$N_3P_3Cl_4(CH_3)(CH_2SiMe_3)$, respectively. Possible explanations for these results are presented. The high polymers formed by these reactions were treated with sodium trifluoroethoxide to yield derivatives in which the hydrolytically sensitive P–Cl bonds were replaced by stable $P{-}OCH_2CF_3$ units. Under certain conditions these substitutions resulted in the concurrent cleavage of the PCH_2–Si side group bonds to yield $P{-}CH_3$ units in their place. Use of this technique has allowed the first synthesis of the polymer $[[NP(OCH_2CF_3)_2]_2{-}[NP(CH_3)_2]]_n$. The behavior of the cyclotetrasiloxane side group under siloxane polymerization conditions is also discussed. The characterization, structure, and properties of the high polymers are also described.

Introduction

Poly(organophosphazenes)[2-9] and the poly(organosiloxanes)[10] constitute two of the main classes of inorganic backbone polymers. Poly(organosiloxanes) have an inherently flexible backbone and a hydrophobicity and thermooxidative stability associated with the presence of alkyl or aryl groups attached to silicon atoms. The properties of poly(organophosphazenes) also result from a high backbone flexibility, mediated by the size and polarity of the side groups attached to the backbone. One of our objectives is to prepare macromolecules that combine some of the characteristics of poly(organosiloxanes) and poly(organophosphazenes).

Three methods can be envisaged for the preparation of hybrid macromolecules that contain both organosilicon and organophosphazene units. The first involves copolymerization reactions between cyclotriphosphazene and cyclosiloxane species to yield main-chain hybrid structures. We have studied the reaction between $(NPCl_2)_3$ and $(OSiMe_2)_3$[11] and showed that cleavage of Si–O bonds by P–Cl bonds is the main reaction pathway. This leads to the formation of cross-linked and hydrolytically unstable species. The second method makes use of reactions that link organosilicon groups to a preformed polyphosphazene backbone. This method, currently being developed by Wisian-Neilson and co-workers,[12] involves an organometallic deprotonation of poly(methylphosphazenes), followed by treatment of the resultant carbanions with organosilicon species, such as Me_3SiCl, to yield phosphazene backbone polymers with methyl and organosilicon side groups. The third method involves the ring-opening polymerization of cyclotriphosphazenes that bear organosilicon side groups. This is the subject of the present paper.

We have reported recently the synthesis of a number of cyclotriphosphazenes (**1**–**9**) that bear organosilicon side groups.[13] All these compounds possess a $P{-}CH_2{-}Si$ linkage unit between the phosphazene and organosilicon components. This linkage unit was selected because of its prospective stability both under hydrolytic conditions and under the rather severe thermal conditions required for the ring-opening polymerization of cyclophosphazenes (or cyclosiloxanes). For example it was already known that cyclophosphazenes that bear alkyl,[14] aryl,[15,16] carboranyl,[17,18] or ferrocenyl[19] side groups linked to the phosphazene ring through P–C bonds will undergo ring-opening polym-

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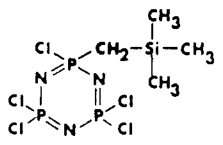

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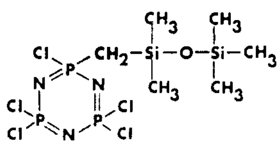

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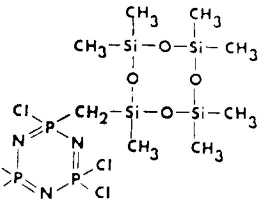

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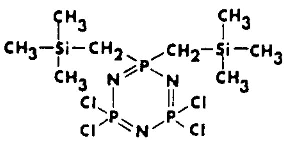

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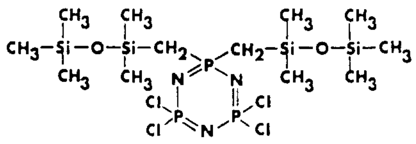

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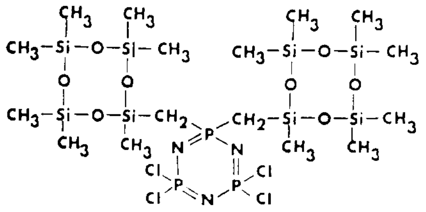

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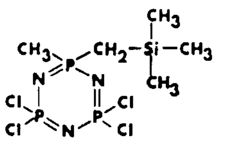

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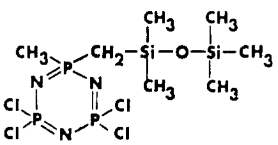

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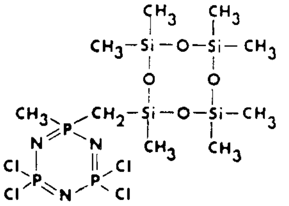

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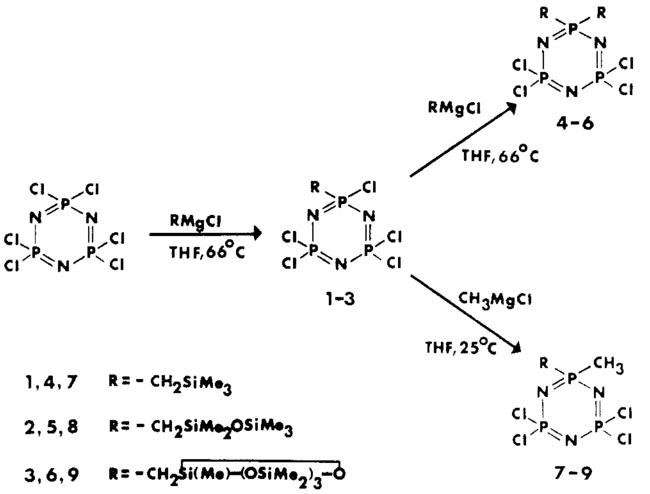
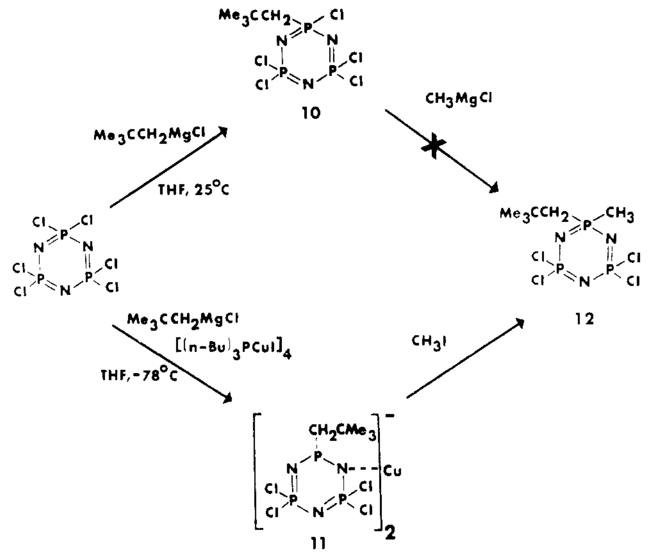
Scheme I



Scheme II



erization without loss of the organic or organometallic side group. By contrast, side groups connected through P–O–C or P–NR–C linkages may be lost at elevated temperatures.[20-22]

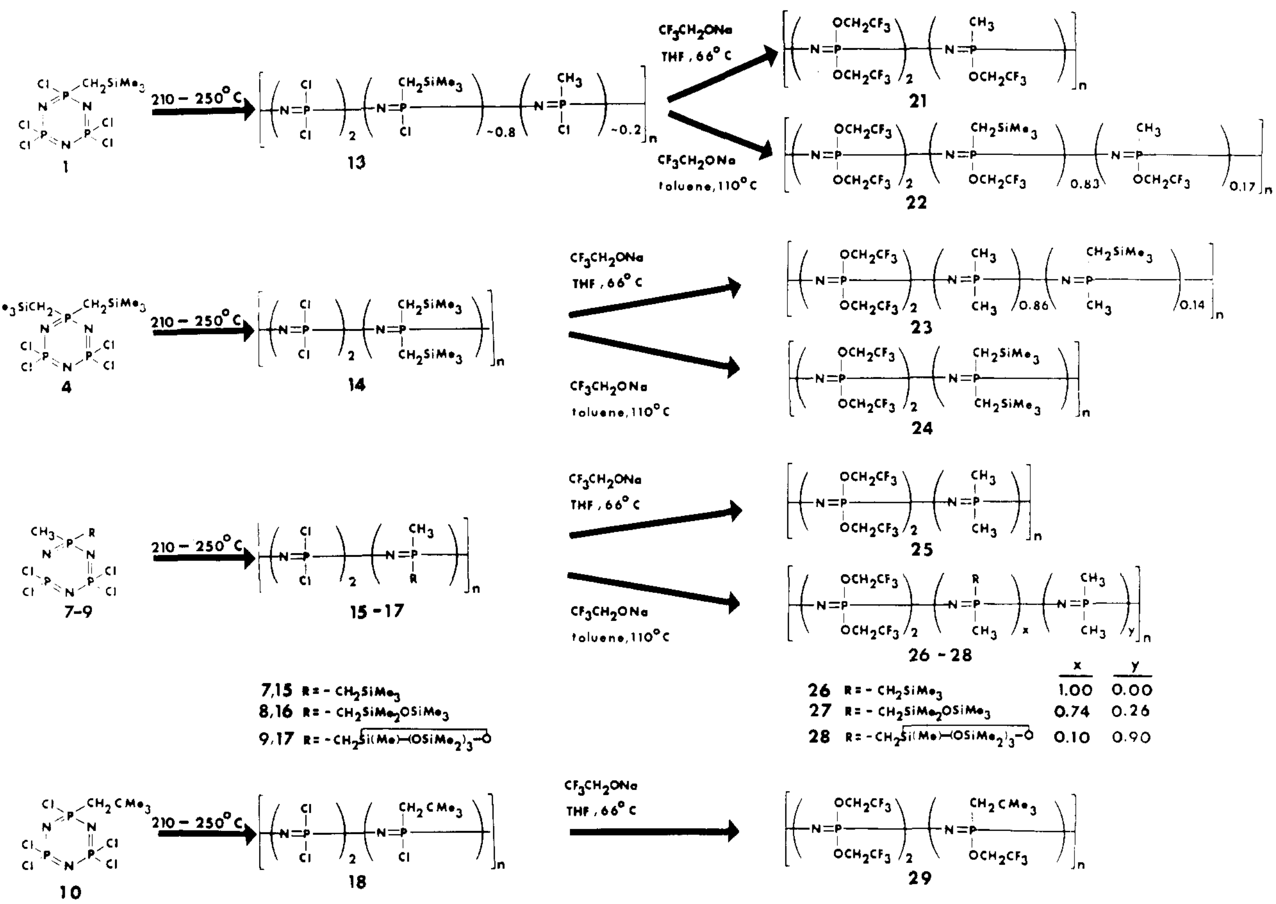
The main objectives of this work were to answer the following questions: (1) Will cyclophosphazenes such as 1–9 undergo phosphazene ring-opening polymerizations at elevated temperatures, and will the cyclosiloxane rings in 3, 6, and 9 polymerize independently of the phosphazene rings? (2) How stable are the organosilicon side groups during both thermal polymerization and the subsequent nucleophilic substitutions needed to replace P–Cl bonds by, for instance, P–O–CH_2CF_3 units? (3) What changes in the properties of polyphosphazenes are brought about by the introduction of organosilyl side groups?

Results and Discussion

Synthesis of Organosilylcyclotriphosphazenes 1–9 and the Neopentylcyclotriphosphazenes 10 and 12. Species 1–9 were synthesized by reaction of the organosilyl Grignard reagents, Me_3SiCH_2MgCl, $Me_3SiOSiMe_2CH_2MgCl$, and $O(SiMe_2O)_3Si(Me)CH_2MgCl$, with $(NPCl_2)_3$ in THF solvent.[13] The method is summarized in Scheme I. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, reacts with 1 equiv of RMgCl [R = CH_2SiMe_3, $CH_2SiMe_2OSiMe_3$, and $CH_2Si(Me)(OSiMe_2)_3O$ in THF at 66 °C to yield the monosubstituted species 1–3. Compounds 1–3 react with more RMgCl to yield the geminally disubstituted compounds 4–6 or react with CH_3MgCl at 25 °C to yield 7–9. The mechanism of the reaction between $(NPCl_2)_3$ and the organosilyl Grignard reagents has been discussed previously.[13]

Synthesis of the neopentyl-substituted cyclotriphosphazenes 10 and 12 was carried out with the use of methods that we have reported previously.[23,24] Mono-

Scheme III



neopentylpentachlorocyclotriphosphazene (**10**) was prepared by the reaction between $(NPCl_2)_3$ and Me_3CCH_2MgCl in THF at 25 °C (Scheme II). It is known that the reactions between $(NPCl_2)_3$ and bulky Grignard reagents such as t-C_4H_9MgCl or i-C_3H_7MgCl yield a monoalkylpentachlorocyclotriphosphazene.[23] The formation of **10** appears to follow the same pattern.[23,25] Treatment of **10** with methylmagnesium chloride did not yield **12**, *gem*-$N_3P_3Cl_4(CH_3)(CH_2CMe_3)$, but rather gave products that were attributed to decomposition of this species. However, **12** was prepared by the reaction between $(NPCl_2)_3$ and neopentylmagnesium chloride in the presence of $[(n\text{-}Bu)_3PCuI]_4$ in THF at −78 °C, followed by treatment with methyl iodide. The anionic metallophosphazene intermediate, **11**, is formed first. This yields **12** on reaction with methyl iodide. The reaction between $(NPCl_2)_3$ and alkyl or aryl Grignard reagents in the presence of $[(n\text{-}Bu)_3PCuI]_4$ has been studied extensively.[13,24,26-28] The method used to prepare **12** is identical with that used to synthesize other dialkyltetrachlorocyclotriphosphazenes.[24] The neopentyl-substituted cyclotriphosphazenes **10** and **12** were prepared to allow a direct comparison to be made between the polymerization of $N_3P_3Cl_5CH_2CMe_3$ (**10**) or *gem*-$N_3P_3Cl_4(CH_3)(CH_2CMe_3)$ (**12**) and their organosilicon analogues $N_3P_3Cl_5CH_2SiMe_3$ (**1**) and *gem*-$N_3P_3Cl_4(CH_3)(CH_2SiMe_3)$ (**4**).

Polymerizations. Six of these compounds underwent phosphazene ring-opening polymerization, and five did not. Those that did not underwent side group decomposition reactions before significant ring-opening polymerization could occur. The following sections will cover the polymerization processes, stabilization of the polymers by replacement of the chlorine atoms by organic side groups, and characterization of the polymers. Those phosphazenes that underwent side-group decomposition in preference to polymerization (**2**, **3**, **5**, **6**, and **12**) will be discussed at the end, together with possible reasons for their behavior.

Table I
Polymerization Results for Compounds 1–9[a]

cyclotriphosphazene	R group CH_2SiMe_3	 CH_2SiMe_2-$OSiMe_3$	 $CH_2Si(Me)$-$(OSiMe_2)_3O$
$N_3P_3Cl_5R$ (**1–3**)	yes	no	no
gem-$N_3P_3Cl_4R_2$ (**4–6**)	yes	no	no
gem-$N_3P_3Cl_4(CH_3)(R)$ (**7–9**)	yes	yes	yes

[a] Yes indicates that cyclotriphosphazene polymerization occurred, and no indicates that it did not.

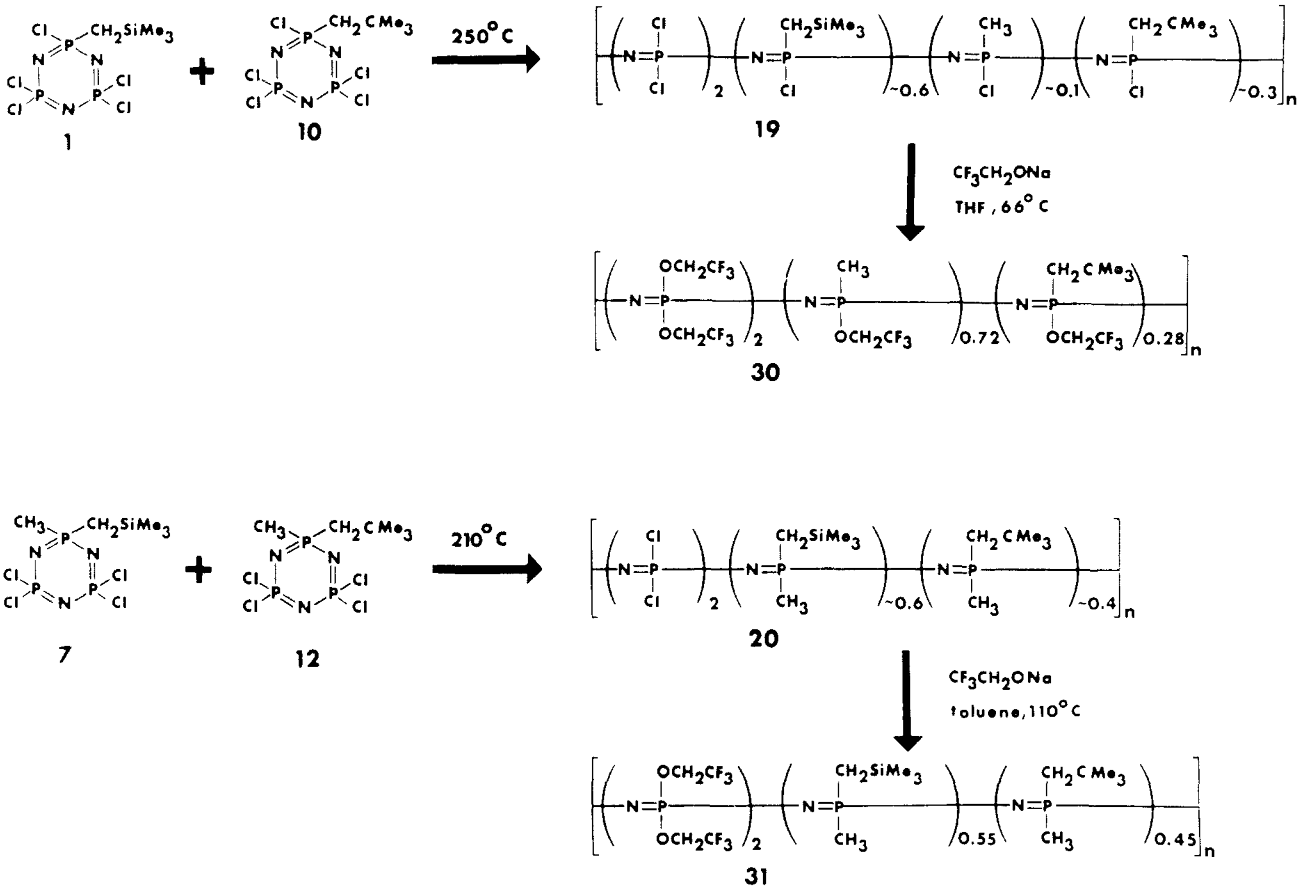
Table II
Summary of Polymerization Data for Compounds 1, 4, 7–9, and 10

cyclotriphosphazene	temp, °C	time, h	approx conv, %[a]
$N_3P_3Cl_5CH_2SiMe_3$ (**1**)	210	24–36	70–80
	250	3–5	
gem-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (**4**)	210	~72	<10
	250	8–10	
gem-$N_3P_3Cl_4(CH_3)(CH_2SiMe_3)$ (**7**)	210	2–5	50–60
	250	<1	
gem-$N_3P_3Cl_4(CH_3)$-$(CH_2SiMe_2OSiMe_3)$ (**8**)	210	2–5	50–60
	250	<1	
gem-$N_3P_3Cl_4(CH_3)[CH_2$-$Si(Me)(OSiMe_2)_3O]$ (**9**)	210	13–17	50–60
	250	2–4	
$N_3P_3Cl_5CH_2CMe_3$ (**10**)	210	>144	70–80
	250	~72	

[a] Percent conversion of cyclic trimer to high polymer.

Compounds **1**, **4** and **7–10** polymerized when heated at 210–250 °C to yield polyphoshazenes **13–18** (Scheme III).

Scheme IV



The results are summarized in Tables I and II.

A direct comparison of the polymerization reactivities of these compounds is difficult because two of the species (**1** and especially **4**) are on the borderline between systems where polymerization is faster than side-group reactions and those with the opposite characteristics. Thus, during the polymerization of **1**, cross-linking occurs after 70–80% reaction together with a minimal amount of PCH_2–Si bond cleavage by P–Cl groups to give P–CH_3 units and Me_3SiCl (this reaction is discussed later). However, species **4** undergoes cross-linking and side group reactions even before 10% conversion has occurred. Nevertheless, an approximate order of ring-opening polymerization reactivity was estimated to be **7** ≈ **8** > **9** > **1** > **4** > **10**.

Following polymerization, the residual cyclic trimers, **1**, **4**, and **7–10** were removed unchanged. No evidence of ring–ring equilibration or organosilicon cleavage products was detected on the basis of ^1H and ^{31}P NMR analyses of the recovered trimers.

Compounds **4** and **7–9** are among the few geminally disubstituted diorganochlorocyclotriphosphazenes that undergo polymerization. The other example is a *gem*-$N_3P_3Cl_4(CH_3)$(*o*-carboranylmethylene) compound.[18] Other geminal dialkyl- or alkylarylchlorocyclotriphosphazenes generally oligomerize or suffer side-group decomposition at the expense of high polymer formation.[16,29] This leads to the conclusion that the organosilicon groups in **4** and **7–9** are especially stable compared to simple alkyl groups.

The neopentylcyclotriphosphazenes, **10** and **12**, also constitute a special case, and the relationship to the organosilicon derivatives **1** and **7** will be obvious. Compound **10** underwent ring-opening polymerization in a manner that was comparable to that of **1** (but without the organosilicon-related side reactions). However, the organosilicon species **1** polymerized much faster (1–4 h at 250 °C) than did the neopentyl compound **10** (~72 h) (Table II). On the other hand, species **12** did not yield high polymers under the reaction conditions chosen but formed oligomeric phosphazene species instead. Compound **7** gave high polymer under identical conditions. Both **10** and **12** copolymerized with the corresponding organosilicon analogue, **1** or **7**, to yield polymers **19** and **20** (Scheme IV).

Chlorine Replacement and Carbon–Silicon Bond Cleavage in the Presence of Sodium Trifluoroethoxide. High polymers **13–20** are sensitive to atmospheric moisture because of the presence of P–Cl bonds. Thus, an essential final step in the synthesis procedure was the replacement of these units by P–OCH_2CF_3 groups by treatment with an excess of sodium trifluoroethoxide.[2,3] However, carbon–silicon and oxygen–silicon bonds can also be cleaved by base,[13,30,31] and a key question was the degree to which P–Cl rather than C–Si or O–Si bonds would react with sodium trifluoroethoxide. The results are summarized in Schemes III and IV.

The mechanistic pathway followed depends mainly on the reaction conditions and particularly on the polarity of the solvent.[13] Phosphorus–chlorine *and* carbon–silicon bond-cleavage reactions occurred rapidly in tetrahydrofuran solvent at 66 °C. By contrast, P–Cl bond cleavage is the predominant reaction in toluene at 110 °C. This allows the structure of the final product to be controlled to give either of two important new polymer types—those bearing trifluoroethoxy and organosilicon side groups or those that bear trifluoroethoxy and methyl side groups—with subtle variations possible depending on the choice of the organosilicon side group.

Species **23** bears mainly trifluoroethoxy and methyl side groups, but 5–10% of the CH_2SiMe_3 groups remained uncleaved, even after forcing reaction conditions in THF. The proposed structure for **24** is based on ^{31}P NMR, ^1H

Table III
Characterization Data

compound	molecular weight M_w	molecular weight M_n	T_g, °C	elem anal.	found	calcd
$[[NP(OCH_2CF_3)_2]_2-[NP(OCH_2CF_3)(CH_3)]]_n$[a] (**21**)	$>2 \times 10^6$	1.3×10^5	−63	C	20.33 (19.94)	20.48
	(1×10^6)	(4.4×10^5)	(−63)	H	1.93 (2.02)	2.04
				N	6.49 (6.39)	6.51
				Cl	0.06 (0.13)	
$[[NP(OCH_2CF_3)_2]_2-[NP(OCH_2CF_3)(CH_2SiMe_3)]_{0.83}-[NP(OCH_2CF_3)(CH_3)]_{0.17}]_n$ (**22**)	$>2 \times 10^6$	3.2×10^5	−61	C	22.58	22.98
				H	2.65	2.81
				N	5.97	5.96
				Cl	0.09	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)_2]_{0.86}-[NP(CH_3)(CH_2SiMe_3)]_{0.14}]_n$ (**23**)	5.7×10^5	8.3×10^4	−54	C	21.15	21.90
				H	2.65	2.67
				N	7.49	7.36
				Cl	0.06	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_2SiMe_3)_2]]_n$ (**24**)	$>2 \times 10^6$	2.5×10^5	−40	C	24.46[b]	27.23
				H	3.68[b]	4.29
				N	7.33[b]	5.96
				Cl	0.58	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)_2]]_n$ (**25**, from **15**)	8.8×10^5	5.3×10^4	−58	C	21.51	21.40
				H	2.65	2.52
				N	7.62	7.49
				Cl	0.10	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)_2]]_n$ (**25**, from **16**)	9.4×10^5	1.2×10^5	−57	C	21.52	21.40
				H	2.60	2.52
				N	7.48	7.49
				Cl	0.06	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)(CH_2SiMe_3)]]_n$ (**26**)	7.5×10^5	8.6×10^4	−55	C	24.20	24.65
				H	3.21	3.51
				N	6.63	6.64
				Cl	0.17	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)(CH_2SiMe_2OSiMe_3)]_{0.74}-[NP(CH_3)_2]_{0.26}]_n$ (**27**)	5.1×10^5	8.4×10^4	−58	C	23.96	24.58
				H	3.44	3.67
				N	6.21	6.28
				Cl	0.48	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)CH_2\overline{Si(Me)(OSiMe_2)_3O}]_{0.10}-[NP(CH_3)_2]_{0.90}]_n$ (**28**)	1.9×10^5	2.4×10^4	−53	C	21.77	21.81
				H	2.70	2.74
				N	7.36	7.13
				Cl	0.20	
$[[NP(OCH_2CF_3)_2]_2-[NP(OCH_2CF_3)(CH_2CMe_3)]]_n$ (**29**)	3.6×10^5	1.9×10^4	−54	C	25.20	25.69
				H	3.03	3.02
				N	6.09	5.99
				Cl	0.25	
$[[NP(OCH_2CF_3)_2]_2-[NP(OCH_2CF_3)(CH_3)]_{0.72}-[NP(OCH_2CF_3)(CH_2CMe_3)]_{0.28}]_n$ (**30**)	$>2 \times 10^6$	2.5×10^5	−60	C	21.65	22.02
				H	2.22	2.33
				N	6.29	6.36
				Cl	0.28	
$[[NP(OCH_2CF_3)_2]_2-[NP(CH_3)(CH_2SiMe_3)]_{0.55}-[NP(CH_3)(CH_2CMe_3)]_{0.45}]_n$ (**31**)	8.2×10^5	4.7×10^4	−50	C	25.12	25.80
				H	3.41	3.55
				N	6.97	6.71
				Cl	0.21	

[a] Values in parentheses for **21** prepared from $N_3P_3Cl_5CH_3$. [b] Although satisfactory elemental analysis could not be obtained, the NMR data (Table IV) gave strong evidence for the structure of this polymer. The values reported are typical of results from several analyses.

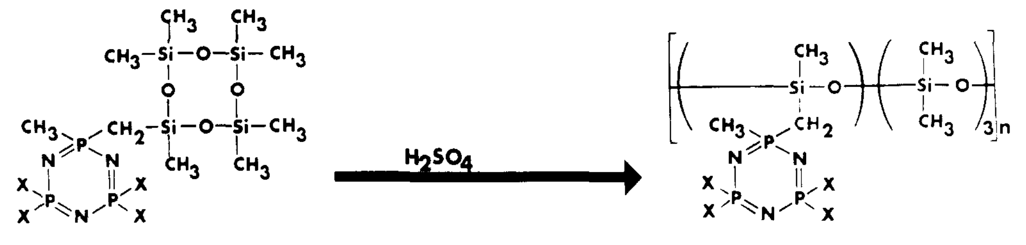
NMR, and infrared spectral data. However, the microanalytical data for **24** were consistent with a structure in which some of the trimethylsilyl residues had been replaced by methyl groups. The ability of sodium trifluoroethoxide in toluene to cleave the PCH_2–Si bond in **15**–**17** depended on the type of organosilicon side group present, as shown in Scheme III. Polymer **15** was resistant to PCH_2–Si bond cleavage, **16** underwent approximately 25% PCH_2–Si bond cleavage, but **17** underwent ~90% cyclosiloxane removal. Presumably, O–Si bond cleavage also occurs concurrently with **16** and **17**.

This synthesis method provides an alternative route to a polymer prepared previously. Polymer **21** can also be prepared by the polymerization of $N_3P_3Cl_5CH_3$, followed by treatment with sodium trifluoroethoxide.[14] The compounds prepared by the two routes were identical in characterization features (NMR and infrared spectra, glass transitions temperatures, etc.) and physical properties. Polymer **25** has not yet been prepared by the polymerization of *gem*-$N_3P_3Cl_4(CH_3)_2$:[32] thus, the present route provides the only access to this macromolecule.

The weight-average (M_w) and number-average (M_n) molecular weights of the trifluoroethoxy derivatives were estimated by gel permeation chromatography. The M_w values ranged from $>10^6$ to 10^5, while the M_n values were between 10^5 and 10^4. These are similar to the values found for other trifluoroethoxyphosphazene polymers.[14,16] The molecular weight distributions were very broad, with polydispersity values between 2 and 20.

Properties of the Polymers. All the trifluoroethoxy-substituted derivatives were elastomers, with glass transition temperatures (T_g) between −63 and −40 °C (see Table III). The silyl and siloxy side groups appeared to have roughly the same influence on the polymer physical properties as did alkyl groups.[14,16] For example, the single-substituent polymer, $[NP(OCH_2CF_3)_2]_n$, is a microcrystalline, film- and fiber-forming material with a T_g of −66 °C. Alkyl, silyl, or siloxy substituents at every third

Scheme V



9 X = Cl

32 X = OCH$_2$CF$_3$

33

X = OCH$_2$CF$_3$

X ≠ Cl

n = 25

phosphorus atom (on the average) remove the propensity for crystallization and allow the elastomeric character associated with the highly flexible backbone to become manifest.

Cyclosiloxane Polymerization. As mentioned earlier, species such as *gem*-$N_3P_3Cl_4(CH_3)[CH_2Si(Me)(OSiMe_2)_3O]$ (**9**) and *gem*-$N_3P_3(OCH_2CF_3)_4(CH_3)[CH_2Si(Me)(OSiMe_2)_3O]$ (**32**) offer the prospect of a *siloxane* ring-opening polymerization. Such a reaction would yield a polysiloxane chain or macrocycle with cyclophosphazene side groups. In addition, species of structure **3**, **6**, or **9** could form the basis of graft-type polysiloxane–polyphosphazene macromolecules derived directly from one "monomer". Thus, a few preliminary experiments were carried out to determine if cyclosiloxane polymerization could be carried out in the presence of the cyclophosphazene side groups.

Sulfuric acid is a well-known initiator for the conversion of $(OSiMe_2)_4$ to high molecular weight $(OSiMe_2)_n$. As a control reaction it was first confirmed that polysiloxanes with $M_w \approx 2 \times 10^5$, n = 2000–3000, were formed from $(OSiMe_2)_4$ in the presence of H_2SO_4 under the reaction conditions chosen (see Experimental Section). Under the same conditions compound **32** yielded a mixture of cyclosiloxane oligomers ($n \approx 25$) of formula **33** (Scheme V). Species **9** could not be induced to undergo oligomerization or polymerization under the same conditions. Use of the basic initiator, Me_4NOH, also failed to induce the polymerization of **9** and **32** even though $(OSiMe_2)_4$ polymerizes readily under the same conditions.

It is possible that the P–Cl and P–OCH_2CF_3 groups in **9** or **32** react with H_2SO_4 or Me_4NOH, thus destroying the initiator. It was found that the presence of $(NPCl_2)_3$ inhibited the polymerization of $(OSiMe_2)_4$ by H_2SO_4 or Me_4NOH. The Me_4NOH-initiated polymerization was also inhibited by $[NP(OCH_2CF_3)_2]_3$. The H_2SO_4-induced polymerization of $(OSiMe_2)_4$ was retarded but not inhibited by $[NP(OCH_2CF_3)_2]_3$.

Competing Reactions That Impair Ring-Opening Polymerization. As mentioned earlier, compounds **2**, **3**, **5**, **6**, and the neopentyl derivative **12** did not yield linear high polymers when heated at 210–250 °C. Instead, competing reactions that lead to side-group reactions, cyclomatrix cross-linking, or oligomerization take place in preference to polymerization. These results fall into a general pattern that is emerging from a wide variety of organophosphazene polymerization attempts being carried out in our laboratory.

The competing reactions fall into the following categories. (1) The presence of non-halogen substituent groups attached to the phosphazene ring, especially two bulky organic groups on the same phosphorus, tends to lower the degree of polymerization that can be achieved. It is assumed that bulky side groups, when at chain ends, reduce the efficiency of chain propagation and may also change the position of the ring–polymer equilibrium to favor oligomers rather than high polymers. The behavior of the neopentyl derivative, **12**, may fall into this category, as may species **3**, **5**, and **6**.

(2) Decomposition of alkyl side groups can occur at high temperatures for phosphazene cyclic trimers that bear both chloro and certain alkyl side groups. These reactions, which may involve dehydrochlorination processes, yield dark colored products and lead to general reorganization and fragmentation of the molecules. Such processes compete effectively against polymerization in the cases of compounds **12**, *gem*-$N_3P_3Cl_4(CH_3)(R')$ (R′ = alkyl or aryl),[29] $N_3P_3Cl_5(t\text{-}C_4H_9)$,[14] and $N_3P_3Cl_5(i\text{-}C_3H_7)$.[14] It is emphasized that reactions of this type appear to be less prevalent with the organosiloxylmethylene–cyclotriphosphazene species than for simple alkylcyclotriphosphazenes.

(3) In the silicon-containing systems reported in this paper, an opportunity exists for PCH_2–Si or O–Si bonds in the side group of one molecule to be cleaved by a P–Cl bond from another molecule. For example, during the conversion of **1** to polymer **13**, Me_3SiCl was eliminated, and some of the $P(Cl)(CH_2SiMe_3)$ groups in the polymer were converted to $P(Cl)(CH_3)$ units. ^{31}P NMR analysis of the polymers showed peaks at 13.5 and 12.6 ppm (less intense) that were attributed to these two groups. Similarly, ^1H NMR analysis indicated that both PCH_3 and PCH_2SiMe_3 groups were present in **13** and the trifluoroethoxy derivative **22**.

This is a minor side reaction for **1** but a major reaction for compounds **2**, **3**, **5**, and **6**, which rapidly formed cross-linked matrices as small-molecule organosilicon species were released. Compounds Me_3SiCl and $Me_3SiOSiMe_3$ were evolved during the heating of **2** or **5**, and various chlorosiloxy compounds were formed from **3** or **6**. These products are almost certainly formed when O–Si bonds are cleaved by P–Cl units, as demonstrated earlier by the reactions of $(NPCl_2)_3$ with $(OSiMe_2)_3$ or $Me_3SiOSiMe_3$.[11]

Thus, the conclusion is reached that those cyclic trimers that can be polymerized to well-defined, linear-type high polymers may be unique only in the sense that the side reactions are slower in those systems. Clearly, the design of future cyclic trimers for polymerization studies must take these facts into account.

Experimental Section

Materials. Hexachlorocyclotriphosphazene was kindly provided by Ethyl Corporation and was purified by recrystallization from hexane and sublimation at 50 °C (0.05 mmHg). Neopentyl chloride, trimethylchlorosilane, and methyl iodide were obtained from Aldrich and were used as received. Resublimed magnesium (Alfa Products) was used as received. Trifluoroethanol (Halocarbon Products) was dried over 3-Å molecular sieves before use. Sodium hydride (Aldrich) was washed several times with dry THF to remove mineral oil and was stored in a drybox before use. The reagent, $[(n\text{-Bu})_3\text{PCuI}]_4$, was prepared by standard methods.[33] Tetrahydrofuran (THF) and toluene were dried over sodium benzophenone ketyl and were distilled under an atmosphere of dry nitrogen before use. Solvents used for the precipitations of poly(trifluoroethoxyphosphazenes) were used without further purification. All reactions were carried out under an atmosphere of dry nitrogen.

Analytical Techniques. ^{31}P (^{1}H decoupled) NMR spectra were obtained with a JEOL FX90Q NMR spectrometer operated at 36.2 MHz. ^{31}P NMR chemical shifts are relative to 85% H_3PO_4 at 0 ppm with positive shift values downfield from the reference. ^{1}H NMR spectra were recorded with the use of a Bruker WP-200 NMR spectrometer operated at 200 MHz. Chemical shifts are relative to tetramethylsilane at δ 0. ^{13}C NMR (^{1}H decoupled) spectra were recorded with the use of a JEOL FX90Q NMR spectrometer operated at 22.5 MHz. All spectra were referenced to internal tetramethylsilane at 0 ppm. Infrared spectra were obtained with the use of a Perkin-Elmer 283B grating spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Knoxville, TN.

Gel permeation chromatography (GPC) was carried out with the use of a Hewlett-Packard HP1090 liquid chromatograph with an HP1037A refractive index detector, an HP3392A integrator, and an HP9121 disk drive. The system was controlled by a Hewlett-Packard HP85B computer. Sample concentrations were approximately 3% by weight and a typical injection volume was 50 μL. Tetrahydrofuran with 0.1% tetra-*n*-butylammonium bromide was used as the eluent for all of the trifluoroethoxy-substituted polyphosphazenes. The columns consisted of Polymer Laboratories Ltd. PL gel 10 μ. Three columns (10^6, 10^6, and 10^3 Å), each with a length of 30 cm, were used along with a precolumn filter. Typical analyses were conducted with an attenuation of 5 (32 mV), a chart speed of 1 cm/min, a peak width of 0.04 min, a threshold of 3, and slice width of 1 s by using Option 14 on the HP 3392 integrator. The HP 1037A refractive index detector was used with positive or negative polarity, a range of 4×10^{-3} RIU, and a temperature of 40 °C. A flow rate of 1 mL/min and pressure of 50 bar were used. The weight-average (M_w) and number-average (M_n) molecular weights were calculated with the use of HP85B computer by using software provided by Hewlett-Packard for the HP1090A GPC system. M_w and M_n were calculated according to the formula $M_w = \sum(\text{Area}_i \cdot M_i)/\sum(\text{Area}_i)$ and $M_n = \sum(\text{Area}_i)/\sum(\text{Area}_i/M_i)$ where Area$_i$ is the area of slice i and m_i is the molecular weight corresponding to slice i. The instrument was calibrated with narrow molecular weight polystyrene standards (Waters Associates) by using THF with 0.1% $(n\text{-Bu})_4\text{NBr}$ as the eluent. Therefore, the molecular weight values are considered to be approximate for the poly(trifluoroethoxyphosphazenes).[34] Glass transition temperatures (Tg) were measured with the use of a Perkin-Elmer DSC 7 and a TAC 7 controller. The data were recorded for samples (approximately 10–20 mg) in crimped aluminum pans with a heating rate of 10 °C/min and helium flow rate of 10 mL/min. The instrument was calibrated with a cyclohexane standard with thermal transitions at −87.06 and 6.54 °C.

Synthesis of 1–9. These compounds were prepared by synthetic techniques described previously.[13] The solid cyclotriphosphazene compounds were recrystallized twice from pentane chilled with dry ice or from hot hexane, followed by two vacuum sublimations at 0.05 mmHg before use in polymerization studies. Liquid samples were vacuum distilled twice before use. All the chlorocyclotriphosphazenes were stored in a drybox before use.

Synthesis of $N_3P_3Cl_5CH_2CMe_3$ (10). Neopentylmagnesium chloride was prepared by the addition of neopentyl chloride (8.7 g, 0.082 mol) to magnesium (2.4 g, 0.10 mol) in dry THF (40 mL). A crystal of iodine was added and the reaction mixture was refluxed at 66 °C for 4 h. After this time the solution discolored and boiled vigorously. When cooled, the solution was transferred to an addition funnel under nitrogen via a double-tipped syringe needle. The THF solution of neopentylmagnesium chloride was then added dropwise to a solution of $(NPCl_2)_3$ (20.0 g, 0.0576 mol) in dry THF (500 mL) over a 1-h period. The reaction mixture was then stirred at 25 °C for 18 h. Solvent was removed under reduced pressure, and diethyl ether (500 mL) was added to the residue. The mixture was washed with 5% HCl (3 × 250 mL), the organic solution was then dried over $MgSO_4$, filtered, and evaporated under reduced pressure to yield crude **10** as an oil. Crude **10** was vacuum distilled twice at 80 °C (0.05 mmHg) to yield pure **10** as a clear liquid. Yield 12.5 g, 56%.

Characterization data for **10**: ^{31}P NMR ($CDCl_3$) AB_2 spin pattern (ν_A, 40.5 ppm; ν_B, 20.2 ppm; J_{PNP}, unresolved); ^{1}H NMR ($CDCl_3$) δ 2.31 ($PCH_2C(CH_3)_3$, dt, 2 H, $J_{PCH} = 17.6$, $J_{PNPCH} = 4.5$ Hz), 1.19 ($PCH_2C(CH_3)_3$, s, 9 H); ^{13}C NMR ($CDCl_3$) ν 51.33 ($PCH_2C(CH_3)_3$, dt, $J_{PC} = 117.8$, $J_{PNPC} = 6.7$ Hz), 30.60 ppm ($PCH_2C(CH_3)_3$, d, $J_{PCCC} = 10.5$ Hz); IR 1230–1170 (vs, P–N), 1470, 1460, 1380, 1370 (m, C–H), 2975 cm^{-1} (s, C–H); MS calcd for $C_5H_{11}Cl_5N_3P_3$ 383, found 383 (Cl_5 isotope pattern). Anal. Calcd for **10**: C, 15.66; H, 2.90; N, 10.96. Found: C, 16.04; H, 2.56; N, 11.00.

Synthesis of *gem*-$N_3P_3Cl_4(CH_3)(CH_2CMe_3)$ (12). A solution of neopentylmagnesium chloride was prepared from neopentyl chloride (21.6 g, 0.203 mol) and magnesium (6.4 g, 0.26 mol) in THF (50 mL) as described above. The Grignard solution was added dropwise to a solution of $(NPCl_2)_3$ (15.00 g, 0.0431 mol) and $[(n\text{-Bu})_3\text{PCuI}]_4$ (9.00 g, 0.0057 mol) in dry THF (300 mL) at −78 °C under an atmosphere of nitrogen. The reaction mixture was then stirred for 16 h, as the temperature was allowed to rise to 25 °C. Methyl iodide (29.8 g, 0.21 mol) was added dropwise to the reaction mixture at 0 °C. The reaction mixture was then stirred at 25 °C for 24 h. The product was isolated as described for **10** above, using toluene as the extraction solvent. The crude product **12** was recrystallized twice from hexane to yield pure **12** as a white solid. Compound **12** sublimed at 70 °C (0.05 mmHg). Yield 8.5 g, 54%; mp 93 °C.

Characterization Data for **12**: ^{31}P NMR ($CDCl_3$) AB_2 spin pattern (ν_A 35.7, ν_B 16.9 ppm; J_{PNP} unresolved); ^{1}H NMR ($CDCl_3$) δ 1.66 (PCH_3, dt, 3 H, $J_{PCH} = 13.9$, $J_{PNPCH} = 1.7$ Hz), 1.87 ($PCH_2C(CH_3)_3$, dt, 2 H, $J_{PCH} = 12.3$, $J_{PNPCH} = 3.4$ Hz), 1.17 ($PCH_2C(CH_3)_3$, s, 9 H); ^{13}C NMR ($CDCl_3$) ν 22.32 (PCH_3, dt, $J_{PC} = 91.5$, $J_{PNPC} = 2.6$ Hz), 46.18 ($PCH_2C(CH_3)_3$, dt, $J_{PC} = 91.5$, $J_{PNPC} = 4.3$ Hz), 31.24 ppm ($PCH_2C(CH_3)$, d, $J_{PCCC} = 8.5$ Hz); IR 1300–1100 (vs, P–N), 1460, 1360 (m, C–H), 2950 cm^{-1} (s, C–H); MS calcd for $C_6H_{14}Cl_4N_3P_3$ 363, found 363 (Cl_4 isotope pattern). Anal. Calcd for **12**: C, 19.85; H, 3.90; N, 11.58. Found: C, 19.80; H, 3.76; N, 11.24.

Polymerization Technique. The cyclic trimers **1–10** and **12** were purified by multiple recrystallization, sublimation, and distillation techniques before use in polymerization reactions. All the trimers were stored in a drybox before use.

Pyrex glass polymerization tubes with a length of 180 mm, outside diameter of 12 mm, and wall thickness of 2 mm, with a constriction 30 mm long and 30 mm from the open end (1–4 g polymerization reactions), or tubes with a length of 200 mm, outside diameter of 20 mm, and wall thickness of 1 mm, with a constriction 40 mm long and 30 mm from the open end (>4 g polymerization reactions), were cleaned and dried in an oven at 130 °C for 24–48 h before use. The tubes were transferred to a drybox and filled with the appropriate trimer. The tubes and contents were evacuated for 30 min at 0.05 mmHg, sealed off at the constriction, wrapped in a wire mesh screen, and heated in a thermoregulated oven (fitted with a mechanical tube rocker) at temperatures between 210–250 °C. Generally, the tubes were removed from the oven when the viscosity of the molten reaction mixture was very high, and the mixture was almost immobile. The tubes were then allowed to cool to room temperature and opened in a nitrogen-filled drybag, and the entire contents (cyclic and polymeric species) were then transferred to the reaction flask for analysis or chlorine replacement reactions with sodium trifluoroethoxide.

Polymerization of $N_3P_3Cl_5CH_2SiMe_3$ (1). Compound **1** (2.00 g, 0.00500 mol) was sealed in a polymerization tube as described above. The tube was heated at 250 °C for 3–5 h or at 210 °C for ~36 h. After this time the clear colorless contents of the tube became highly viscous but not immobile. A typical conversion of **1** to high polymer **13** was approximately 70%, as determined by ^{31}P NMR spectroscopy and recovery of unchanged **1**.

Polymerization of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)_2$ (4). Compound **4** (10.0 g, 0.0222 mol or 2.26 g, 0.00500 mol) was sealed in a polymerization tube as described above. The tube was heated at 250 °C or 210 °C for approximately 8–10 h or ~72 h, respectively. The tubes were removed from the oven when the contents became yellow and *slightly* viscous. (Cross-linking occurs rapidly after this point.) The conversion of **4** to **14** was estimated to be <10% on the basis of ^{31}P NMR analysis and recovery of unreacted **4**.

Polymerization of *gem*-$N_3P_3Cl_4(CH_3)(R)$ [R = CH_2SiMe_3 (7), $CH_2SiMe_2OSiMe_3$ (8), and $CH_2\overline{Si(Me)(OSiMe_2)_3O}$] (9). Compound **7**, **8**, or **9** (0.005 mol) was sealed in a polymerization tube as described previously. The tubes were heated at 210 °C for approximately 2–5 h (**7** and **8**) or 18 h (**9**). The tubes were removed from the oven when the contents were light yellow or clear and were highly viscous (but not immobile). The conversion of **7–9** to **15–17** was approximately 50–60% in all cases as determined by ^{31}P NMR spectroscopy and recovery of residual **7–9**.

Polymerization of $N_3P_3Cl_5CH_2CMe_3$ (10). Compound **10** (1.92 g, 0.00500 mol) was sealed in a polymerization tube as described above. The tube was heated at 250 °C for 72 h, after which time the contents of the tube were dark in color and viscous. The conversion of **10** to **18** was estimated to be approximately 70% as determined by ^{31}P NMR spectroscopy.

Copolymerization of $N_3P_3Cl_5CH_2SiMe_3$ (1) and $N_3P_3Cl_5CH_2CMe_3$ (10). Compounds **1** (1.00 g, 0.0025 mol) and **10** (0.96 g, 0.0025 mol) were sealed in a polymerization tube as described previously. The tube was heated at 250 °C for approximately 5 h, after which time the contents of the tube were highly viscous but not immobile. Analysis of the cyclic and polymeric products by ^{31}P NMR spectroscopy suggested that approximately 40–50% of the cyclic species were converted to high polymer **19**. Significantly more residual **10** than **1** was detected.

Copolymerization of *gem*-$N_3P_3Cl_4(CH_3)(CH_2SiMe_3)$ (7) and *gem*-$N_3P_3Cl_4(CH_3)(CH_2CMe_3)$ (12). Compounds **7** (0.95 g, 0.0025 mol) and **12** (0.91 g, 0.0025 mol) were sealed in a polymerization tube and heated at 210 °C for approximately 5 h. After this period the contents of the tube were light yellow and highly viscous but not immobile. Approximately 70–80% of the cyclic species was converted to copolymer **20** as determined by ^{31}P NMR spectroscopy. The residual cyclic species consisted primarily of compound **12**.

Attempted Polymerization of 2, 3, 5, and 6. Compounds **2**, **3**, **5**, and **6** (0.005 mol) were sealed in Pyrex tubes as described previously. The contents of the tubes were heated at 210–250 °C until a highly viscous (but not immobile) melt was observed (in the case of **5**, the contents of the tube became immobile almost immediately). When cooled to room temperature, the tubes were opened in a nitrogen-filled drybag, and the contents were transferred to a dry reaction flask. Volatile species such as Me_3SiCl and $Me_3SiOSiMe_3$ (from **2** and **5**) and $ClSiMe_2(OSiMe_2)_{1-4}Cl$ (from **3** and **6**) were removed under vacuum and collected in a trap at −196 °C. Gas chromatographic analysis was used to identify these species. Part of the polymeric residue dissolved in dry THF and was analyzed by ^{31}P NMR spectroscopy, which provided evidence for residual cyclic trimers **2**, **3**, **5**, and **6**.

Attempted Polymerization of 12. Compound **12** gave a low molecular weight oligomeric species when heated at 210 or 250 °C for 72 h. Severe darkening occurred. ^{31}P NMR analysis of the partially soluble products derived from **12** showed that no residual **12** remained and that a complex mixture of cyclic and linear species was present (multiple resonances detected at 50 to 40 ppm, 18 to 14 ppm, and −19 to −31 ppm). The reaction products were treated with sodium trifluoroethoxide to convert these species to stable trifluoroethoxy derivatives. Analysis by gel permeation chromatography (GPC) showed that only low molecular weight species were present ($M_w < 10^5$).

Polymer Substitution Reactions with Sodium Trifluoroethoxide in Toluene. (a) Synthesis of 22, 26–28, and 31. A solution of sodium trifluoroethoxide in toluene was prepared by the slow dropwise addition of CF_3CH_2OH (6.60 g, 0.0660 mol) to NaH (1.44 g, 0.0600 mol) in dry toluene (250 mL). On completion of addition, the reaction mixture was heated to reflux for 4–5 h to ensure that CF_3CH_2ONa had formed completely. The trimer/polymer mixture of **1/13**, **7–9/15–17**, or **7,12/20** (0.005 mol) was dissolved in dry toluene (100 mL) and then transferred to an addition funnel via a double-tipped syringe needle. This solution was added dropwise to the refluxing solution of CF_3CH_2ONa in toluene at 110 °C over a 1–2-h period. On completion of addition, the reaction mixture was heated at 110 °C for an additional 10 h, and during this time the trifluoroethoxy-substituted polymer precipitated. The reaction mixture was allowed to cool to 25 °C and the insoluble material allowed to settle. The supernatant toluene solution was removed by decantation via a double-tipped syringe needle, and a solution of Me_3SiCl (6.5 g, 0.060 mol) in dry THF (250 mL) was added to the residue. The polymeric material dissolved after stirring for 6 h. The solvent and volatile species were removed under reduced pressure, acetone (250 mL) was added to the residue, and the mixture was shaken or stirred until the polymer redissolved. The acetone solution was concentrated under reduced pressure and water was added to precipitate the polymer and dissolved most of the salts. The polymer was purified further by reprecipitation from a concentrated solution in acetone or THF into water (twice) and pentane (3 times) and then Soxhlet extracted with pentane for 48 h. The polymer was dried under vacuum for 72 h to yield **22**, **26–28**, and **31** as light brown, film-forming elastomers. Yields (based on 0.005 mol of chlorocyclotriphosphazene) were 20–30%. Complete characterization data are given in Tables III and IV.

(b) Synthesis of 24. A solution of sodium trifluoroethoxide in toluene was prepared by the slow dropwise addition of CF_3CH_2OH (39.0 g, 0.390 mol) to Na (6.12 g, 0.266 mol) in dry toluene (1 L). On completion of addition the reaction mixture was heated to reflux for 4–5 h. The mixture of **4** and **14** (10.0 g, 0.0222 mol) was dissolved in dry toluene (250 mL). The procedure described in (a) was followed. The quantity of Me_3SiCl (19.7 g, 0.181 mol) in dry THF (1 L) was increased for the neutralization of sodium trifluoroethoxide. Polymer **24** is a white, fibrous material. The yield was <10%. Complete characterization is given in Tables III and IV.

Polymer Substitution Reactions with Sodium Trifluoroethoxide in THF. (a) Synthesis of 21, 25, 29, and 30. A solution of sodium trifluoroethoxide in THF was prepared by the slow dropwise addition of CF_3CH_2OH (8.25 g, 0.0825 mol) to NaH (1.80 g, 0.0750 mol) in dry THF (100 mL) cooled to 0 °C. On completion of addition the solution was stirred until evolution of hydrogen had ceased and a clear solution was obtained (<1 h). The trimer/polymer mixture of **1/13**, **7–8/15–16**,[35] **10/18**, or **1,10/19** (0.005 mol) was dissolved in dry THF (100 mL), transferred to an addition funnel, and then added dropwise to the hot CF_3CH_2ONa solution at 66 °C over a 1–2-h period. The solution was stirred at 66 °C for 24 h. The reaction mixture was allowed to cool to 25 °C, and Me_3SiCl was added until the solution was acidic to wet litmus. The solvent and volatile materials were then removed under reduced pressure. The polymers were isolated and purified as described above. Yields were approximately 20–30%. Complete characterization data for **21**, **25**, **29**, and **30** are given in Tables III and IV.

(b) Synthesis of 23. A solution of CF_3CH_2ONa in THF was prepared as described above using CF_3CH_2OH (11.0 g, 0.110 mol) and NaH (2.4 g, 0.100 mol). The trimer/polymer mixture of **4/14** (2.26 g, 0.00500 mol) in dry THF (100 mL) was added dropwise to the refluxing solution of CF_3CH_2ONa. The reaction mixture was refluxed at 66 °C for 48 h and the polymer was isolated as described in (a) above. Polymer **23** is a light brown, film-forming elastomer. The yield was <10%. Complete characterization is given in Tables III and IV.

^{31}P NMR and ^1H NMR Analysis of the Cyclic and Polymeric Products from the Polymerization of 1, 4, 7–9, 10, 1/10, and 7/12. Two tubes containing either **1**, **4**, **7–9**, **10**, **1/10**, or **7/12** were heated as described previously. The first tube was opened in a nitrogen-filled glovebag and transferred to a vacuum sublimator. The residual cyclic species **1**, **4**, **7–9**, **10**, or **12** were sublimed or distilled from the polymer at 100 °C (0.05 mmHg) and were analyzed by ^1H NMR and ^{31}P NMR spectroscopy. These analyses showed that the cyclic species were recovered unchanged. No higher cyclic species were formed and no cleavage of the organosilicon group occurred during the polymerization process.

Table IV
NMR Data

	^{31}P NMR[a,f]		^{1}H NMR[b,c,f]			
compound	signal	chem shift, ppm	signal	chem shift, δ	proton ratio[d]	J_{PCH},[g] Hz
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(Cl)(CH_2SiMe_3}]_{\sim 0.8}\text{–}[\mathrm{NP(Cl)(CH_3)}]_{\sim 0.2}]_n$ (**13**)	$\mathrm{PCl_2}$	−22.3, −23.2 (m)	$\mathrm{PC}H_3$, $\mathrm{PC}H_2\mathrm{SiMe_3}$	1.54 (m)	2–3 H	
	P(Cl)(C)	13.5, 12.6 (m)	$\mathrm{PCH_2Si}Me_3$	0.18 (m)	7–8 H	
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(CH_2SiMe_3)_2}]]_n$ (**14**)	$\mathrm{PCl_2}$	−30.7 (s)	$\mathrm{PC}H_2\mathrm{SiMe_3}$	1.53 (d)	4 H	16.5
	$\mathrm{P(C)_2}$	20.9 (s)	$\mathrm{PCH_2Si}Me_3$	0.29 (s)	18 H	
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(CH_3)(CH_2SiMe_3)}]]_n$ (**15**)	$\mathrm{PCl_2}$	−28.6 (t)	$\mathrm{PC}H_3$	1.60 (d)	3 H	13.8
	$\mathrm{P(C)_2}$	18.9 (p)	$\mathrm{PC}H_2\mathrm{SiMe_3}$	1.20 (d)	2 H	14.1
			$\mathrm{PCH_2Si}Me_3$	0.21 (s)	9 H	
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(CH_3)\text{-}(CH_2SiMe_2OSiMe_3)}]]_n$ (**16**)	$\mathrm{PCl_2}$	−28.3 (t)	$\mathrm{PC}H_3$	1.69 (d)	3 H	14.1
	$\mathrm{P(C)_2}$	17.6 (p)	$\mathrm{PC}H_2\mathrm{SiMe_2OSiMe_3}$	1.40 (d)	2 H	18.5
			$\mathrm{PCH_2Si}Me_2\mathrm{OSiMe_3}$	0.37 (s)	6 H	
			$\mathrm{PCH_2SiMe_2OSi}Me_3$	0.14 (s)	9 H	
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(CH_3)CH_2\text{-}}\overline{\mathrm{Si(Me)(OSiMe_2)_3O}}]]_n$ (**17**)	$\mathrm{PCl_2}$	−28.0 (t)	$\mathrm{PC}H_3$	1.75 (d)	3 H	14.3
	$\mathrm{P(C)_2}$	16.7 (p)	$\mathrm{PC}H_2\mathrm{Si}$	1.61(d)	2 H	18.9
			$\mathrm{PCH_2Si}Me$	0.56 (s)	3 H	
			$(\mathrm{OSi}Me_2)_3$	0.27 (s)	6 H	
				0.24 (s)	6 H	
				0.21 (s)	3 H	
				0.20 (s)	3 H	
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(Cl)(CH_2CMe_3)}]]_n$ (**18**)	$\mathrm{PCl_2}$	−22.3 (m)	$\mathrm{PC}H_2\mathrm{CMe_3}$	2.12 (br)	2 H	
	P(Cl)(C)	9.4 (m)	$\mathrm{PCH_2C}Me_3$	1.14 (br)	9 H	
$[[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(Cl)(CH_2SiMe_3)}]_{\sim 0.6}\text{–}[\mathrm{NP(Cl)(CH_3)}]_{\sim 0.1}\text{–}[\mathrm{NP(Cl)\text{-}(CH_2CMe_3)}]_{\sim 0.3}]_n$ (**19**)	$\mathrm{PCl_2}$	−23.2 (m)	$\mathrm{PC}H_3$, $\mathrm{PC}H_2\mathrm{SiMe_3}$	1.55 (br)	1–2 H	
	P(Cl)(C)	13.4, 12.5, 9.4 (m)	$\mathrm{PCH_2Si}Me_3$	0.19 (br)	5–6 H	
			$\mathrm{PC}H_2\mathrm{CMe_3}$	2.13 (br)	~1 H	
			$\mathrm{PCH_2C}Me_3$	1.08 (br)	2–3 H	
$[\mathrm{NPCl_2}]_2\text{–}[\mathrm{NP(CH_3)(CH_2SiMe_3)}]_{\sim 0.6}\text{–}[\mathrm{NP(CH_3)(CH_2CMe_3)}]_{\sim 0.4}]_n$ (**20**)	$\mathrm{PCl_2}$	−28.6 (m)	$\mathrm{P(C}H_3\mathrm{)(CH_2SiMe_3)}$	1.60 (d)	1–2 H	13.3
	$\mathrm{P(C)_2}$	18.9, 16.2 (m)	$\mathrm{P(CH_3)(C}H_2\mathrm{SiMe_3)}$	1.09 (d)	1–2 H	16.5
			$\mathrm{P(CH_3)(CH_2Si}Me_3\mathrm{)}$	0.21 (s)	5–6 H	
			$\mathrm{P(C}H_3\mathrm{)(CH_2CMe_3)}$	1.57 (d)	1–2 H	12.5
			$\mathrm{P(CH_3)(C}H_2\mathrm{CMe_3)}$	1.72 (d)	~1 H	13.9
			$\mathrm{P(CH_3)(CH_2C}Me_3\mathrm{)}$	1.09 (s)	3–4 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(OCH_2CF_3)\text{-}(CH_3)}]]_n$ (**21**)	$\mathrm{P(O)_2}$	−8.2 (m)	$\mathrm{PC}H_3$	1.79 (d)	3 H	16.9
	P(O)(C)	18.5 (m)	$\mathrm{POC}H_2\mathrm{CF_3}$	4.52 (m)	10 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(OCH_2CF_3)\text{-}(CH_2SiMe_3)}]_{0.83}\text{–}[\mathrm{NP(OCH_2CF_3)\text{-}(CH_3)}]_{0.17}]_n$ (**22**)	$\mathrm{P(O)_2}$	−9.9 (m)	$\mathrm{PC}H_3$	1.79 (d)	0.5 H	16.9
	P(O)(C)	21.6 (m)	$\mathrm{PC}H_2\mathrm{SiMe_3}$	1.54 (d)	1.7 H	21.0
			$\mathrm{PCH_2Si}Me_3$	0.18 (s)	7.5 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.53 (m)	10 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_3)_2}]_{0.86}\text{–}[\mathrm{NP(CH_3)(CH_2SiMe_3)}]_{0.14}]_n$ (**23**)	$\mathrm{P(O)_2}$	−7.6 (m)	$\mathrm{P(C}H_3\mathrm{)_2}$	1.67 (d)	5.2 H	14.3
	$\mathrm{P(C)_2}$	15.6 (m)	$\mathrm{P(C}H_3\mathrm{)(C}H_2\mathrm{SiMe_3)}$	not detected[e]		
			$\mathrm{P(CH_3)(CH_2Si}Me_3\mathrm{)}$	0.19 (s)	1.3 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.48 (m)	8 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_2SiMe_3)_2}]]_n$ (**24**)	$\mathrm{P(O)_2}$	−11.5 (m)	$\mathrm{PC}H_2\mathrm{SiMe_3}$	1.49 (d)	4 H	16.8
	$\mathrm{P(C)_2}$	20.6 (m)	$\mathrm{PCH_2Si}Me_3$	0.21 (s)	18 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.49 (m)	8 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_3)_2}]]_n$ (**25**)	$\mathrm{P(O)_2}$	−7.6 (m)	$\mathrm{PC}H_3$	1.67 (d)	6 H	14.3
	$\mathrm{P(C)_2}$	15.6 (m)	$\mathrm{POC}H_2\mathrm{CF_3}$	4.48 (m)	8 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_3)\text{-}(CH_2SiMe_3)}]]_n$ (**26**)	$\mathrm{P(O)_2}$	−9.2 (m)	$\mathrm{PC}H_3$	1.71 (d)	3 H	14.0
	$\mathrm{P(C)_2}$	18.5 (m)	$\mathrm{PC}H_2\mathrm{SiMe_3}$	1.43 (d)	2 H	18.0
			$\mathrm{PCH_2Si}Me_3$	0.19 (s)	9 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.48 (m)	8 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_3)\text{-}(CH_2SiMe_2OSiMe_3)}]_{0.74}\text{–}[\mathrm{NP(CH_3)_2}]_{0.26}]_n$ (**27**)	$\mathrm{P(O)_2}$	−9.1 (m)	$\mathrm{P(C}H_3\mathrm{)_2}$	1.67 (d)	1.6 H	14.0
	$\mathrm{P(C)_2}$	17.3 (m), 15.5 (m)	$\mathrm{P(C}H_3\mathrm{)(CH_2SiMe_2OSiMe_3)}$	1.72 (d)	2.2 H	14.3
			$\mathrm{P(CH_3)(C}H_2\mathrm{SiMe_2OSiMe_3)}$	1.50 (d)	1.5 H	18.7
			$\mathrm{P(CH_3)(CH_2Si}Me_2\mathrm{OSiMe_3)}$	0.29 (s)	4.4 H	
			$\mathrm{P(CH_3)(CH_2SiMe_2OSi}Me_3\mathrm{)}$	0.09 (s)	6.7 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.47 (m)	8 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_3)CH_2\text{-}}\overline{\mathrm{Si(Me)(OSiMe_2)_3O}}]_{0.10}\text{–}[\mathrm{NP(CH_3)_2}]_{0.90}]_n$ (**28**)	$\mathrm{P(O)_2}$	−7.6	$\mathrm{P(C}H_3\mathrm{)_2}$	1.67 (d)	5.4 H	14.3
	$\mathrm{P(C)_2}$	15.6 (m)	$\mathrm{P(C}H_3\mathrm{)(C}H_2\mathrm{Si)}$	not detected[e]		
			$\mathrm{SiC}H_3$	0.16 (s)	1.9 H	
				0.12 (s)		
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.48 (m)	8 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(OCH_2CF_3)\text{-}(CH_2CMe_3)}]]_n$ (**29**)	$\mathrm{P(O)_2}$	−9.7 (m)	$\mathrm{PC}H_2\mathrm{CMe_3}$	2.09 (d)	2 H	10.4
	P(O)(C)	17.7 (m)	$\mathrm{PCH_2C}Me_3$	1.14 (s)	9 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.51 (m)	10 H	
$[[\mathrm{NP(OCH_3CF_3)_2}]_2\text{–}[\mathrm{NP(OCH_2CF_3)\text{-}(CH_3)}]_{0.72}\text{–}[\mathrm{NP(OCH_2CF_3)\text{-}(CH_2CMe_3)}]_{0.28}]_n$ (**30**)	$\mathrm{P(O)_2}$	−8.8 (m)	$\mathrm{PC}H_3$	1.79 (d)	2.2 H	16.8
	P(O)(C)	18.1 (m)	$\mathrm{PC}H_2\mathrm{CMe_3}$	2.11 (d)	0.6 H	14.0
			$\mathrm{PCH_2C}Me_3$	1.13 (s)	2.5 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.52 (m)	10 H	
$[[\mathrm{NP(OCH_2CF_3)_2}]_2\text{–}[\mathrm{NP(CH_3)\text{-}(CH_2SiMe_3)}]_{0.55}\text{–}[\mathrm{NP(CH_3)\text{-}(CH_2CMe_3)}]_{0.45}]_n$ (**31**)	$\mathrm{P(O)_2}$	−9.3 (m)	$\mathrm{P(C}H_3\mathrm{)(CH_2SiMe_3)}$	1.71 (d)	1.6 H	13.9
	$\mathrm{P(C)_2}$	18.6 (m), 16.4 (m)	$\mathrm{P(CH_3)(C}H_2\mathrm{SiMe_3)}$	1.43 (d)	1.1 H	17.9
			$\mathrm{P(CH_3)(CH_2Si}Me_3\mathrm{)}$	0.19 (s)	4.9 H	
			$\mathrm{P(C}H_3\mathrm{)(CH_2CMe_3)}$	1.71 (d)	1.4 H	13.9
			$\mathrm{P(CH_3)(C}H_2\mathrm{CMe_3)}$	1.97 (d)	0.9 H	14.6
			$\mathrm{P(CH_3)(CH_2C}Me_3\mathrm{)}$	1.15 (s)	4.1 H	
			$\mathrm{POC}H_2\mathrm{CF_3}$	4.48 (m)	8 H	

[a] THF solution ($\mathrm{D_2O}$ lock). [b] $\mathrm{C_6D_6}$ solution (chlorophosphazene species). [c] Acetone–d_6 solution (trifluoroethoxy species). [d] Average number of protons per one repeat (3 PN) unit. [e] Not detected due to the low concentration of these protons in the presence of the dominant $\mathrm{P(C}H_3\mathrm{)_2}$ protons at a similar chemical shift δ 1.7–1.4. However, integration of peak areas suggested the presence of these protons. [f] (s) singlet, (d) doublet, (t) triplet, (q) quartet, (p) pentet, (m) multiplet, (br) broad multiplet. [g] Coupling constant.

The quantity of the recovered cyclic species was used as a measure of the approximate conversion to the analogous high polymer (Table II). After the sublimation process, the residual polymeric materials swelled in organic solvents such as dry THF but did not dissolved, and were, therefore, cross-linked.

From the second tube, a portion of the polymer/trimer mixture was dissolved in C_6D_6 and analyzed by ^1H NMR spectroscopy. The ^1H NMR spectra showed distinct resonances for PCH_3, PCH_2Si, $SiCH_3$, PCH_2CMe_3, and $PCH_2C(CH_3)_3$ protons for both the polymeric (Table IV) and trimeric species. No detectable cleavage or rearrangement of the organosilicon or neopentyl groups occurred during the polymerization of **4** to **14**, **7**–**9** to **15**–**17**, **10** to **18**, or **7**/**12** to **20**, since the integration of peak areas showed the relative ratios of protons to be correct. Some cleavage of the organosilicon group was detected during the polymerization of **1** to **13** and **1**/**10** to **19** (see text). The remainder of the contents from the second tube were dissolved in dry THF and analyzed by ^{31}P NMR spectroscopy. The spectra showed resonances for both the cyclic and high polymeric species (Table IV). The conversion of trimer to high polymer (Table II) was also estimated by analysis of the ^{31}P NMR spectra.

Cyclotetrasiloxane Polymerization Reactions. All polymerization or attempted polymerization reactions involving $(OSiMe_2)_4$, **9**, and **32**[13] were carried out in an identical manner. The cyclotetrasiloxane species (1.6 mmol) and H_2SO_4 (0.018 mmol) or Me_4NOH (0.004 mmol) were heated at 90–110 °C under an atmosphere of nitrogen for 24 h. For reactions that made use of $(OSiMe_2)_4$ in the presence of $(NPCl_2)_3$ or $[NP(OCH_3CF_3)_2]_3$, an equivalent amount (1.6 mmol) of these cyclotriphosphazene species was added to the reaction mixture. The H_2SO_4-catalyzed reaction mixtures were worked up by the addition of ethyl acetate (50 mL) and were washed with water (50 mL). Ethyl acetate was removed under reduced pressure to yield the methylsiloxane polymers, oligomers, or residual cyclic species which were analyzed by gel permeation chromatography. The Me_4NOH-catalyzed polymerizations were examined after decomposition of the catalyst at 130 °C and removal of Me_3N and MeOH under vacuum.

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Registry No. **1**, 110718-14-4; **4**, 110718-15-5; **7**, 110718-16-6; **8**, 110718-17-7; **9**, 110718-18-8; **10**, 110718-19-9; **10** (homopolymer), 110718-20-2; **12**, 110718-21-3; (**1**)(**10**) (copolymer), 110718-23-5; (**7**)(**12**) (copolymer), 110718-24-6; Me_3CCH_2MgCl, 13132-23-5; $(NPCl_2)_3$, 940-71-6.

References and Notes

(1) This is the third paper from our laboratory on hybrid organosilicon–organophosphazene chemistry. For the first two papers, see ref 11 and 13.
(2) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(3) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(4) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(5) Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic: New York, 1972.
(6) Allcock, H. R. *Sci. Prog. Oxf.* **1980**, *66*, 355.
(7) Allcock, H. R. *Chem. Eng. News* **1985**, *63* (11), 22.
(8) Tate, D. P. *J. Polym. Sci. Symp.* **1974**, *48*, 33.
(9) Singler, R. E.; Hagnauer, G. L.; Sicka, R. W. *ACS Symp. Ser.* **1984**, *No. 260*, 143.
(10) Hardman, B. B.; Torkelson, A. *Encycl. Chem. Technol. 3rd ed.* **1982**, *20*, 922.
(11) Allcock, H. R.; Brennan, D. J.; Allen, R. W. *Macromolecules* **1985**, *18*, 139.
(12) Wisian-Neilson, P.; Ford, R. R.; Neilson, R. H.; Roy, A. K. *Macromolecules* **1986**, *19*, 2089.
(13) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M.; Parvez, M. *Organometallics* **1986**, *5*, 2434.
(14) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules* **1980**, *13*, 1332.
(15) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.
(16) Allcock, H. R.; Connolly, M. S. *Macromolecules* **1985**, *18*, 1330.
(17) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.
(18) Allcock, H. R.; Scopelianos, A. G.; Whittle, R. R.; Tollefson, N. M. *J. Am. Chem. Soc.* **1983**, *105*, 1316.
(19) Allcock, H. R.; Lavin, K. D.; Riding, G. H. *Macromolecules* **1985**, *18*, 1340.
(20) Allcock, H. R.; Schmutz, J. L.; Kosydar, K. M. *Macromolecules* **1978**, *11*, 179.
(21) Ferrar, W. T.; DiStefano, F. V.; Allcock, H. R. *Macromolecules* **1980**, *13*, 1345.
(22) Allcock, H. R.; Kolich, C. H.; Kossa, W. C. *Inorg. Chem.* **1977**, *16*, 3362.
(23) Allcock, H. R.; Desorcie, J. L.; Harris, P. J. *J. Am. Chem. Soc.* **1983**, *105*, 2814.
(24) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.
(25) The reaction between $(NPCl_2)_3$ and Me_3CCH_2MgCl in the presence of methyl iodide traps out a metallophosphazene intermediate to yield *gem*-$N_3P_3Cl_4(CH_3)(CH_2CMe_3)$, indicating that a metal–halogen exchange process occurs.
(26) Allcock, H. R.; Harris, P. J. *J. Am. Chem. Soc.* **1979**, *101*, 6221.
(27) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.
(28) Allcock, H. R.; Harris, P. J.; Nissan, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 2256.
(29) (a) Allcock, H. R.; Brennan, D. J.; Dunn, B. S.; Parvez, M., manuscript in preparation. (b) Compounds such as *gem*-$N_3P_3Cl_4(CH_3)(R')$ ($R' = CH_3$, C_2H_5, n-C_4H_9, C_6H_5, i-C_3H_7, and t-C_4H_9) undergo decomposition and oligomerization reactions in preference to ring-opening polymerization.
(30) Eaborn, C. *Organosilicon Compounds*; Butterworth: London, 1960.
(31) Roedel, G. F. *J. Am. Chem. Soc.* **1949**, *71*, 269.
(32) It would appear that **25** could be prepared by the treatment of a polymer such as $[[NPCl_2]_2–[NP(CH_3)_2]]_n$ with CF_3CH_2ONa. However, this polymer has never been prepared. Attempts to ring-open polymerize *gem*-$N_3P_3Cl_4(CH_3)_2$ do not yield $[[NPCl_2]_2–[NP(CH_3)_2]]_n$ but rather yield low molecular weight oligomers and decomposition products.[29]
(33) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.
(34) The weight-average (M_w) and number-average (M_n) molecular weight values for $[NP(OCH_2CF_3)_2]_n$ were determined by absolute (light scattering and membrane osmometry) and secondary (GPC with polystyrene standards) methods. The results are as follows. Sample 1: $M_w = 1.07 \times 10^6$, $M_n = 1.56 \times 10^5$ (absolute); $M_w = 1.6 \times 10^6$, $M_n = 1.9 \times 10^5$ (secondary). Sample 2: $M_w = 3.15 \times 10^6$, $M_n = 4.93 \times 10^5$ (absolute); $M_w = 2.8 \times 10^6$, $M_n = 8.2 \times 10^5$ (secondary). The results demonstrate that molecular weight values for poly[(trifluoroethoxy)phosphazenes] can be estimated with use of GPC techniques.
(35) Polymer **25** could not be prepared from **17** [$R = CH_2Si(Me)(OSiMe_2)_3O$] as a consequence of Si–O bond cleavage reactions that resulted in cross-linking.