Synthesis of Polyphosphazenes Bearing Geminal (Trimethylsilyl)methylene and Alkyl or Phenyl Side Groups[1]

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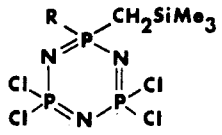
ABSTRACT: The ring-opening polymerization of a series of organosilylcyclophosphazenes of formula *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(R)$, where R = C_2H_5, *i*-C_3H_7, *n*-C_4H_9, *t*-C_4H_9, *neo*-C_5H_{11}, and C_6H_5, is described and is compared with the polymerization behavior of the non-silylated counterparts, *gem*-$N_3P_3Cl_4(CH_3)(R)$. Polymerization is markedly favored by the presence of the organosilicon group. In the organosilyl derivatives, geminal *t*-C_4H_9 or *neo*-C_5H_{11} cosubstituent groups retard polymerization compared to CH_3, C_2H_5, *n*-C_4H_9, or C_6H_5 groups. The *i*-C_3H_7 group has an intermediate effect. It is speculated that the *t*-C_4H_9, *neo*-C_5H_{11}, and *i*-C_3H_7 groups give rise to polymerization-inhibiting side reactions. The polymers prepared by the polymerization of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(R)$ were subjected to chlorine replacement reactions by treatment with sodium trifluoroethoxide. Reactions carried out in toluene solution allowed replacement of chlorine without concurrent attack on the organosilyl groups. In THF solvent, CH_2–Si bond cleavage occurred to replace the (trimethylsilyl)methylene units by methyl groups.

Polymers that contain a phosphazene backbone and organosilicon side groups are of considerable interest as hybrid systems that may combine some of the properties of polyphosphazenes and poly(organosiloxanes).[2-6] Two synthetic routes to polymers of this type are being explored. In one, substitution reactions carried out on the organic side groups of a pre-formed poly(organophosphazene) allow organosiloxane units to be attached to the polymer.[6] In the other, organosilane or organosiloxane groups are first attached to a small-molecule cyclophosphazene, which is then subjected to phosphazene ring-opening polymerization.[3,4] By following this second approach, we reported the preparation of cyclotriphosphazenes with $CH_2SiMe_2OSiMe_3$, $CH_2Si(Me)(OSiMe_2)_3O$ (cyclotetrasiloxane), or CH_2SiMe_3 groups attached to a cyclotriphosphazene ring. Ring-opening polymerization of specific trimers yielded the phosphazene high polymers.

As part of that work, questions arose about the influence on the polymerization of cosubstituents located geminal to the organosilicon side groups. For example, it was found that a methyl group geminal to a $CH_2SiMe_2OSiMe_3$, $CH_2Si(Me)(OSiMe_2)_3O$, or CH_2SiMe_3 group favored polymerization, but two geminal $CH_2SiMe_2OSiMe_3$ or $CH_2Si(Me)(OSiMe_2)_3O$ groups inhibited polymerization, as did a chlorine atom geminal to an organosiloxy group. These influences were ascribed to steric effects and to silicon–oxygen cleavage reactions. Nevertheless, the picture was sufficiently complicated that a closer inspection of the geminal side group effect was needed.

With these facts in mind, we have been able to synthesize a series of phosphazene cyclic trimers with the general structure shown in 1.[5] The only variable within this series of compounds is the group R, geminal to the organosilyl unit. Group R can be ethyl, isopropyl, *n*-butyl, *tert*-butyl, *neo*-pentyl, or phenyl. Together with the compound reported earlier, in which R is methyl,[3,4] these species provide a range of structures to probe the influence of geminal substituents on the polymerization process and on the properties of the polymers formed by this route. In addition, the existence of compounds of type 2, in which the organosilicon unit is replaced by a methyl group, has allowed comparisons to be made of the polymerization behavior of the silyl and non-silyl compounds.



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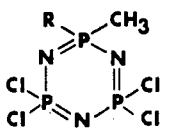

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R = CH_3 (a), C_2H_5 (b), *i*-C_3H_7 (c), *n*-C_4H_9 (d), *t*-C_4H_9 (e), *neo*-C_5H_{11} (f), C_6H_5 (g)

Results and Discussion

Polymerization Reactions. The 14 compounds represented by structures 1 and 2 were synthesized by methods reported previously.[3-5,7,8]

Cyclophosphazenes that bear alkyl or aryl side groups in addition to chloro units can, in principle, participate in three competing reactions when heated at temperatures above 200 °C. The simplest process involves ring-expansion reactions to give higher cyclic oligomers. The second alternative is ring-opening polymerization to give linear or macrocyclic high polymers in which several thousand repeating units may be linked together. In both of these reactions, the organic side groups are inert and the repeating group structure of the cyclic trimer is carried through to the higher oligomers or high polymers. In the third possibility, reactions of the side group occur, often by mechanisms that inhibit the formation of high polymers.

Compounds of type 1, in which R = CH_3, C_2H_5, *n*-C_4H_9, and C_6H_5, underwent ring-opening polymerization when heated at 210 °C (Scheme I). Both the (trimethylsilyl)methylene and the organic side groups survived the reaction conditions and were incorporated into the high polymer (3). An intermediate situation existed when the organic group R was *i*-C_3H_7: polymerization was accompanied by a partial loss of trimethylsilyl units as tri-

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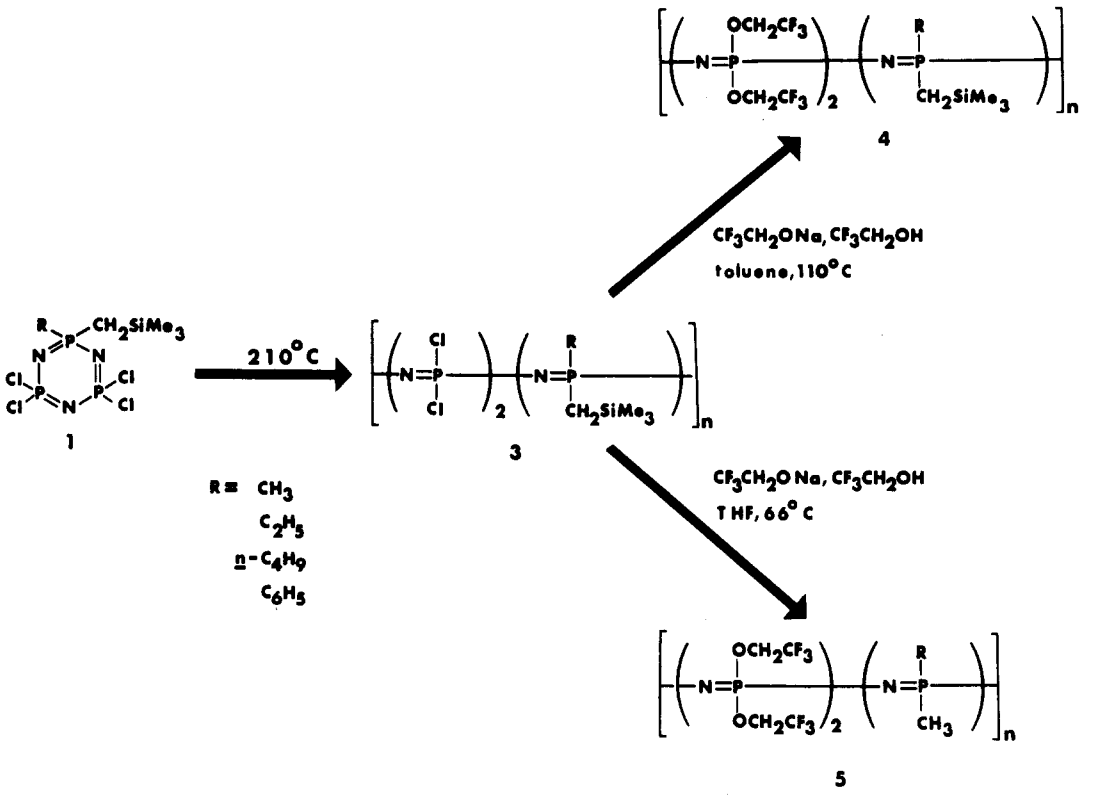
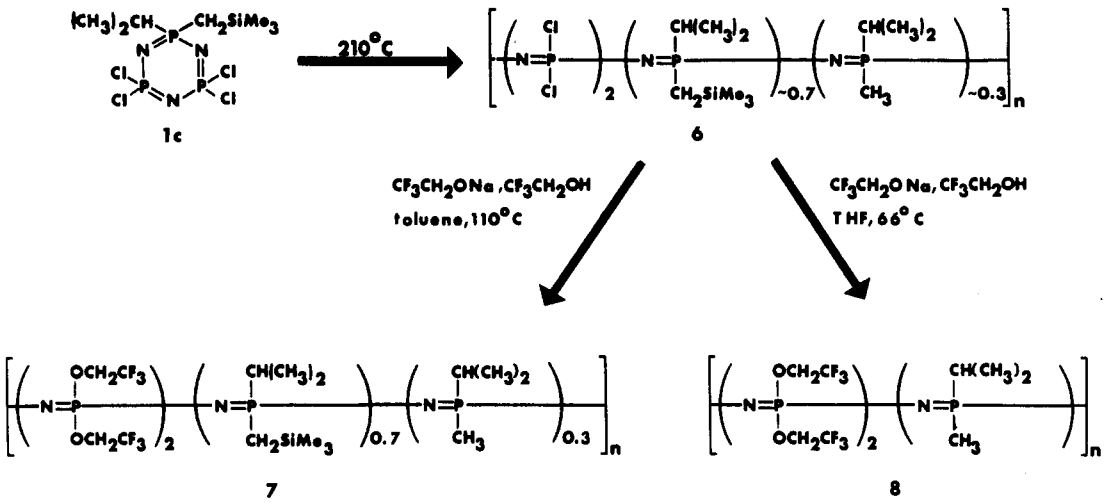
Scheme I



Scheme II

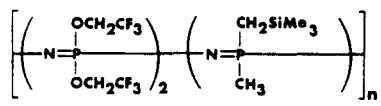


methylchlorosilane. Methyl groups were found at these sites in the final high polymer (6) (Scheme II). Finally, no high polymers were formed when R was t-C_4H_9 or neo-C_5H_{11}. In these cases, complex reactions occurred that included alkyl side group involvement, possibly accompanied by ring-coupling reactions. Brown or black colors appeared during these side reactions. Previous studies have also demonstrated that bulky alkyl side groups give rise to cross-linking, decomposition, and discoloration when the cyclotriphosphazenes are heated.[4,9] The exact mechanism of these side reactions is not known, but t-C_4H_9 or neo-C_5H_{11} groups are expected to be the most sensitive to rearrangement or fragmentation reactions.

Interestingly, none of the trimers of type 2 that possessed a methyl substituent in place of a (trimethylsilyl)methylene group yielded high polymers. The principle products formed when these compounds were heated at 210 °C were a complex mixture of oligomers, side-group-modified products, and hydrogen chloride. This provides a striking illustration of the role played by the (trimethylsilyl)methylene unit in facilitating the polymerization process, at least when the geminal cosubstituent is CH_3, C_2H_5, n-C_4H_9, or C_6H_5. The reason for this protective role by the organosilicon unit is not clear. A steric shielding of, for example, a geminal CH_3 or C_2H_5 group against attack by a P–Cl unit on another molecule is a possibility, as is a shielding of the α-CH bonds in an n-C_4H_9 cosubstituent group. When the organosilicon group is not present, liberation of hydrogen chloride by such reactions may inhibit ring-opening polymerization.[10-13]

Replacement of Chlorine Atoms by Trifluoroethoxy Groups. Polymers such as 3 or 6 are difficult to study because of the hydrolytic instability of the phosphorus–chlorine bonds. Replacement of the chlorine atoms in

Chart I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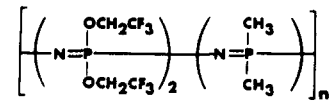
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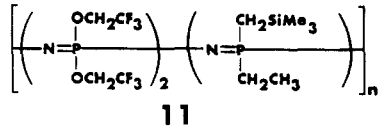
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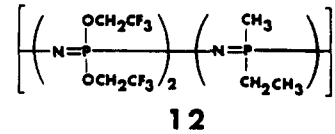
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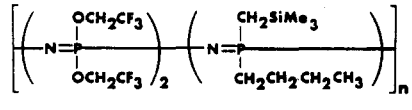
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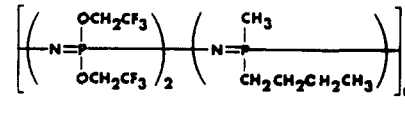
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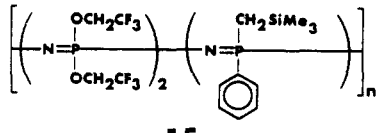
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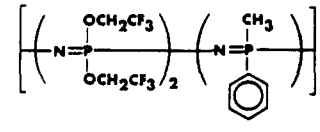
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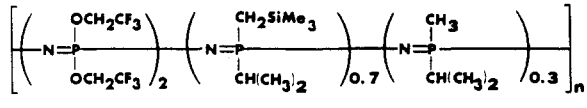
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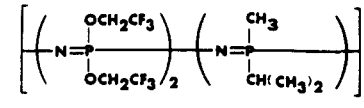
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chlorophosphazene polymers by hydrophobic organic groups, such as trifluoroethoxy or phenoxy units, is the classical method for the stabilization of phosphazene high polymers.[14,15] This method was utilized in the present work also. However, the outcome of the halogen replacement reaction depended on the nature of the reaction solvent employed.

Treatment of high polymers **3** and **6** with sodium trifluoroethoxide in toluene brought about complete replacement of chlorine atoms by trifluoroethoxy groups to give polymers of type **4** or **7**. The organosilicon groups were unaffected by this process. However, when tetrahydrofuran was used as a solvent, chlorine replacement was accompanied by carbon–silicon bond cleavage. After subsequent protonation, the final polymers possessed methyl groups in place of the original (trimethylsilyl)-methylene units (polymers **5** and **8**). This carbon–silicon bond cleavage pathway allows access to polyphosphazenes that bear both trifluoroethoxy and geminal methyl–alkyl or geminal methyl–phenyl side group arrangements. These polymers are inaccessible by the more direct synthesis routes.

Characterization and Properties of the High Polymers. The synthetic procedures described above yielded the 10 high polymers depicted as **7–16**.[16] The structures were determined by ^{31}P and ^{1}H NMR spectroscopy, microanalysis, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC). The data are shown in Tables I–III.

^{31}P NMR spectroscopy of high polymers **7–16** (Table II) provided evidence for resonances for NPR_2 (R = alkyl or CH_2SiMe_3) at 25–19 ppm and $NP(R)(C_6H_5)$ at 12–8 ppm. The resonances for $NP(OCH_2CF_3)_2$ were detected at −7 to −11 ppm. ^{1}H NMR spectroscopy (Table III) revealed that the relative ratio of $POCH_2CF_3$, $PCH_2Si(CH_3)_3$, PCH_3, and PR (R = alkyl and phenyl) protons in the high polymers corresponded to the structures shown. The ratio of NPR_2 to $NP(OCH_2CF_3)_2$ units determined by NMR methods was found to be approximately 1:2. The microanalytical data (Table I) were consistent with the proposed structures: typically less than 1% residual chlorine atoms remained.

The polymers were either elastomers (**9**, **10**, **12**, **14**, and **16**) or flexible film-forming materials (**7**, **8**, **11**, **13**, and **15**) that were soluble in ketonic solvents or in THF. The glass transition temperatures (T_g) of these polymers ranged from −70 to −30 °C. The T_g values for the phenyl-substituted derivatives, **15** and **16**, were 20–30 °C higher than those of their alkyl-substituted counterparts. This probably reflects a decrease in the skeletal torsional flexibility due to the presence of the bulky phenyl groups attached to every third phosphorus atom. The polymers had broad molecular weight distributions, with weight-average (M_w) molecular weight values in the region 10^5–10^6 and number-average (M_n) molecular weight values in the range 10^4–10^5.

Experimental Section

Instrumentation. Gel permeation chromatography (GPC) was carried out with the use of a Hewlett-Packard HP1090 liquid chromatograph with a HP1037A refractive index detector, an HP3392A integrator, and an HP85B computer. Sample concentrations were approximately 3% by weight (in THF) and the typical injection volume was 50 μL for the poly((trifluoroeth-

Table I
Polyphosphazene Characterization Data[a]

compound	R	molecular weight M_w	molecular weight M_n	T_g, °C	elemental anal. found	elemental anal. calcd
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_2SiMe_3)(R)]\}_n$	C_2H_5 (11)	4.5×10^5	1.0×10^4	−62	C 25.62	25.97
					H 3.66	3.74
					N 6.17	6.49
					Cl 0.05	
	n-C_4H_9 (13)	5.2×10^5	1.2×10^4	−57	C 28.12	28.45
					H 4.08	4.19
					N 6.28	6.22
					Cl 0.10	
	C_6H_5 (15)	4.2×10^5	1.3×10^5	−32	C 30.75	31.08
					H 3.60	3.49
					N 6.27	6.04
					Cl 0.05	
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_3)(R)]\}_n$	C_2H_5 (12)	8.5×10^5	7.9×10^4	−67	C 23.11	22.97
					H 2.98	2.81
					N 7.20	7.31
					Cl 0.05	
	i-C_3H_7 (8)	1.7×10^5	2.3×10^4	−53	C 24.55	24.46
					H 3.30	3.09
					N 7.79	7.13
					Cl 0.57	
	n-C_4H_9 (14)	4.2×10^5	7.2×10^4	−64	C 25.59	25.88
					H 3.33	3.35
					N 6.84	6.97
					Cl 0.29	
	C_6H_5 (16)	2.2×10^5	7.0×10^4	−34	C 28.51	28.90
					H 2.62	2.59
					N 6.43	6.74
					Cl 0.54	
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_2SiMe_3)(i\text{-}C_3H_7)]_{0.70}$-$[NP(CH_3)(i\text{-}C_3H_7)]_{0.30}\}_n$	(7)	2.3×10^5	5.4×10^4	−52	C 24.92	26.47
					H 3.63	3.73
					N 6.79	6.57
					Cl 0.53	

[a] See ref 4 for characterization data for **9** and **10** (R = CH_3).

Table II
Polyphosphazene ^{31}P NMR Data[a]

compound	R	signal	chem shift, ppm[d]
$\{[NPCl_2]_2$-$[NP(CH_2SiMe_3)(R)]\}_n$[b]	C_2H_5 (**3b**)	$P(Cl)_2$	−29.8 (m)
		$P(C)_2$	24.1 (m)
	n-C_4H_9 (**3d**)	$P(Cl)_2$	−29.9 (m)
		$P(C)_2$	22.3 (m)
	C_6H_5 (**3g**)	$P(Cl)_2$	−28.1 (m)
		$P(C)_2$	11.1 (m)
$\{[NPCl_2]_2$-$[NP(CH_2SiMe_3)$-$(i\text{-}C_3H_7)]_{\sim 0.7}$-$[NP(CH_3)$-$(i\text{-}C_3H_7)]_{\sim 0.3}\}_n$[b]	(6)	$P(Cl)_2$	−31.4 (m)
		$P(C)_2$	27.3, 24.6 (m)
$\{[NP(OCH_2CF_3)_2]$-$[NP(CH_2SiMe_3)(R)]\}_n$[c]	C_2H_5 (11)	$P(O)_2$	−10.3 (m)
		$P(C)_2$	23.8 (m)
	n-C_4H_9 (13)	$P(O)_2$	−10.5 (m)
		$P(C)_2$	22.0 (m)
	C_6H_5 (15)	$P(O)_2$	−10.0 (m)
		$P(C)_2$	11.4 (m)
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_3)(R)]\}_n$[c]	C_2H_5 (12)	$P(O)_2$	−7.9 (m)
		$P(C)_2$	20.7 (m)
	i-C_3H_7 (8)	$P(O)_2$	−8.3 (m)
		$P(C)_2$	24.2 (m)
	n-C_4H_9 (14)	$P(O)_2$	−8.0 (m)
		$P(C)_2$	19.1 (m)
	C_6H_5 (16)	$P(O)_2$	−7.6 (m)
		$P(C)_2$	8.5 (m)
$\{[NP(OCH_2CF_3)_2$-$[NP(CH_2SiMe_3)$-$(i\text{-}C_3H_7)]_{0.7}$-$[NP(CH_3)$-$(i\text{-}C_3H_7)]_{0.3}\}_n$[c]	(7)	$P(O)_2$	−12.0, −10.4 (m)
		$P(C)_2$	26.4, 24.1 (m)

[a] See ref 4 for ^{31}P NMR spectra for the polymers where R = CH_3 (**3a**, **9**, and **10**). [b] THF solution (D_2O lock). [c] Acetone-d_6 solution. [d] ^{31}P NMR resonances consisted of unresolved multiplets (m) for species **3** and **6**, while complex multiplets were detected for species **7**–**16**.

oxy)phosphazenes). Tetrahydrofuran with 0.1% $(n\text{-Bu})_4NBr$ was used as the eluent. The instrument was calibrated with narrow molecular weight polystyrene standards (Waters Assoc.) using THF with 0.1% $(n\text{-Bu})_4NBr$ as the eluent and with polyphosphazene standards provided by Drs. G. Hagnauer and R. Singler of the US Army Materials Laboratory, Watertown, MA. (Other details regarding the GPC analysis method have been reported elsewhere.[4]) Glass transition temperatures (T_g) were recorded with the use of a Perkin-Elmer DSC 7 instrument with 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.

Polymerization Technique. The cyclic trimers were purified by multiple recrystallization and sublimation techniques and were stored in a drybox before polymerization.

Pyrex glass polymerization tubes with a length of 180 mm, outside diameter of 12 mm, wall thickness of 2 mm, with a constriction of 30 mm long and 30 mm from the open end were cleaned and then 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 Torr, sealed at the constriction, wrapped in a wire mesh screen, and heated at 210 °C in a thermoregulated oven fitted with a mechanical rocker. Generally, the tubes were removed from the oven when the molten reaction mixture was almost immobile. The tubes were then allowed to cool to room temperature and were opened in a nitrogen-filled drybag, and the entire contents (cyclic and polymeric species) were transferred to a reaction flask for analysis or chlorine replacement reactions with sodium trifluoroethoxide.

Polymerization of *gem*-$N_3P_3Cl_4(CH_2SiMe_3)(R)$ (1) [R = C_2H_5 (b), i-C_3H_7 (c), n-C_4H_9 (d), and C_6H_5 (g)]. Compound **1** was sealed in a polymerization tube, as described previously. The tubes were heated at 210 °C for approximately 16 h (R = C_2H_5), 24 h (R = n-C_4H_9 and C_6H_5), and 48–72 h (R = i-C_3H_7).

Table III
Polyphosphazene ^{1}H NMR Data[a,b]

compound	R	signal	chem shift, ppm[c]	coupling constants, Hz
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_2SiMe_3)(R)]\}_n$	C_2H_5 (11)	$PCH_2Si(CH_3)_3$	1.40 (d), 2 H	J_{PCH} = 17.1
		$PCH_2Si(CH_3)_3$	0.20 (s), 9 H	J_{PCCH} = 20.0 (PR)
		PCH_2CH_3	1.96 (m), 2 H	J_{HCCH} = 7.5 (PR)
		PCH_2CH_3	1.20 (dt), 3 H	
		$POCH_2CF_3$	4.49 (m), 8 H	
	n-C_4H_9 (13)	$PCH_2Si(CH_3)_3$	1.40 (d), 2 H	J_{PCH} = 17.5
		$PCH_2Si(CH_3)_3$	0.20 (s), 9 H	J_{HCCH} = 7.2 (PR)
		$P(CH_2)_3CH_3$	2.00–1.30 (m), 6 H	
		$P(CH_2)_3CH_3$	0.92 (t), 3 H	
		$POCH_2CF_3$	4.48 (m), 8 H	
	C_6H_5 (15)	$PCH_2Si(CH_3)_3$	1.74 (d), 2 H	J_{PCH} = 19.0
		$PCH_2Si(CH_3)_3$	−0.04 (s), 9 H	
		PC_6H_5 (ortho)	8.00 (m), 2 H	
		PC_6H_5 (meta, para)	7.44 (m), 3 H	
		$POCH_2CF_3$	4.47 (m), 4 H	
			4.32 (m), 4 H	
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_3)(R)]\}_n$	C_2H_5 (12)	PCH_3	1.62 (d), 3 H	J_{PCH} = 13.8
		PCH_2CH_3	1.87 (m), 2 H	J_{PCCH} = 20.1 (PR)
		PCH_2CH_3	1.17 (dt), 3 H	J_{HCCH} = 7.6 (PR)
		$POCH_2CF_3$	4.48 (m), 8 H	
	i-C_3H_7 (8)	PCH_3	1.62 (d), 3 H	J_{PCH} = 13.4
		$PCH(CH_3)_2$	1.95 (m), 1 H	J_{PCCH} = 18.7 (PR)
		$PCH(CH_3)_2$	1.18 (dd), 6 H	J_{HCCH} = 7.1 (PR)
		$POCH_2CF_3$	4.47 (m), 8 H	
	n-C_4H_9 (14)	PCH_3	1.64 (d), 3 H	J_{PCH} = 14.0
		$P(CH_2)_2CH_2CH_3$	1.96–1.60 (m), 4 H	J_{HCCH} = 7.2 (PR)
		$P(CH_2)_2CH_2CH_3$	1.39 (m), 2 H	
		$P(CH_2)_2CH_2CH_3$	0.91 (t), 3 H	
		$POCH_2CF_3$	4.48 (m), 9 H	
	C_6H_5 (16)	PCH_3	1.77 (dt), 3 H	J_{PCH} = 14.3
		PC_6H_5 (ortho)	7.78 (m), 2 H	
		PC_6H_5 (meta, para)	7.37 (m), 3 H	
		$POCH_2CF_3$	4.37 (m), 8 H	
$\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_2SiMe_3)(i$-$C_3H_7)]_{0.7}$-$[NP(CH_3)(i$-$C_3H_7)]_{0.3}\}_n$	(7)	PCH_2SiMe_3	1.40 (d), 1.4 H	$J_{PCH}(PCH_2SiMe_3)$ = 16.8
		PCH_2SiMe_3	0.20 (s), 6.3 H	$J_{PCH}(PCH_3)$ = 13.4
		PCH_3	1.63 (d), 0.9 H	$J_{PCCH}[PCH(CH_3)_2]$ = 18.8
		$PCH(CH_3)_2$	1.97 (m), 1 H	$J_{HCCH}[PCH(CH_3)_2]$ = 6.7
		$PCH(CH_3)_2$	1.19 (dd), 6 H	
		$POCH_2CF_3$	4.47 (m), 8 H	

[a] See ref 4 for ^{1}H NMR data for the polymers where R = CH_3 (9 and 10). [b] Acetone-d_6 solution. [c] Singlet (s), doublet (d), triplet (t), quartet (q).

The tubes were removed from the oven when the contents were highly viscous. In the case of 1c (R = i-C_3H_7), the contents of the tube became discolored. Decomposition of 1c sometimes occurred instead of polymerization to 6. The conversion of the trimers to the high polymers was approximately 50–70% in all cases, as determined by ^{31}P NMR spectroscopy.

Substitution Reactions Using Sodium Trifluoroethoxide in Toluene. Synthesis of $\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_2SiMe_3)(R)]\}_n$ [R = C_2H_5 (11), n-C_4H_9 (13), and C_6H_5 (15)] and $\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_2SiMe_3)(i$-$C_3H_7)]_{0.7}$-$[NP(CH_3)(i$-$C_3H_7)]_{0.3}\}_n$ (7). 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 appropriate trimer/polymer mixture (1 and 3 or 1c and 6) (0.005 mol) was dissolved in dry toluene (100 mL) and was 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 at 110 °C over a 1–2-h period. On completion of addition, the reaction mixture was heated at 110° for an additional 10 h. During this time, the trifluoroethoxy-substituted polymer precipitated. The reaction mixture was allowed to cool to 25 °C, and the insoluble material was allowed to settle. The supernatant toluene solution was decanted via double-tipped syringe needle. A solution of Me_3SiCl (6.5 g, 0.060 mol) in dry THF (300 mL) was then added to the residue to neutralize the remaining CF_3CH_2ONa. The polymeric material dissolved with stirring within 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 to dissolve most of the salts. The polymeric material was dried under vacuum and was further purified by reprecipitation from a concentrated solution in THF or acetone into water twice and into pentane 3 times. The polymer was Soxhlet-extracted with pentane for 48 h and then dried under vacuum for 72 h. Polymers 11, 13, 15, and 7 were isolated in yields of 20–30% (based on 0.005 mol of chlorocyclotriphosphazene). Complete characterization data are given in Tables I–III.

Substitution Reactions with Sodium Trifluoroethoxide in THF. Synthesis of $\{[NP(OCH_2CF_3)_2]_2$-$[NP(CH_3)(R)]\}_n$ [R = C_2H_5 (12), n-C_4H_9 (14), C_6H_5 (16), and i-C_3H_7 (8)]. 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. The trimer/polymer mixture of 1 and 3 or 1c and 6 (0.005 mol) was dissolved in dry THF (100 mL), transferred to an addition funnel, and then added dropwise to the hot solution of CF_3CH_2ONa in THF 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 in the previous section. Yields were approximately 20–30%. Complete characterization data for 12, 14, 16, and 8 are given in Tables I–III.

Attempted Polymerization of *gem*-$N_3P_3Cl_4(CH_3)(R)$ (2).

Compounds **2** (0.005 mol) were sealed in polymerization tubes, as described previously, and then heated at 210 °C for 6–72 h. During this time, the contents of the tubes became discolored and maintained a constant low viscosity (R = CH_3, C_2H_5, *n*-C_4H_9, *neo*-C_5H_{11}, and C_6H_5). Species **2c** (R = *i*-C_3H_7) became only slightly discolored and slightly viscous, while **2e** (R = *t*-C_4H_9) remained clear and nonviscous after 72 h at 210 °C. (Compound **2c** underwent partial reaction under these conditions while **2e** did not react.) The tubes were opened in a nitrogen-filled drybag, and HCl was detected as a volatile reaction product. The contents of each tube were transferred to a reaction vessel, and dry THF (50 mL) was added. A portion of each product was insoluble in this solvent and appeared to be cross-linked. ^{31}P NMR analysis of the soluble reaction products detected broad resonances at 55–50 ppm (37–35 ppm when R = C_6H_5), −11 to −19 ppm, and −26 to −28 ppm, which suggested that a complex skeletal or side group rearrangement had taken place. ^1H NMR analysis of these products (in C_6D_6 solvent) indicated that the P–CH_3 groups had undergone side reactions at elevated temperatures (a broad resonance at δ 2–1 was detected instead of the "doublet" that is normally associated with PCH_3 protons), while the P–R groups appeared to remain intact. The detection of methyl chloride[17] and hydrogen chloride from these reactions was taken as evidence for side reactions that involved the P–CH_3 units.

Treatment with sodium trifluoroethoxide in THF, under conditions identical with those used for the systems derived from **1**, yielded viscous oils. The molecular weights of these products (determined by gel permeation chromatography) were M_n = 10^3–10^4 and M_w = 10^4–10^5. These values are roughly one-tenth of those found for the products derived from trimers **1**. ^{31}P and ^1H NMR analysis data were compatible with the presence of a complex mixture of products. In particular, changes were evident in the expected P–CH_3 unit resonances. The data lead to the conclusion that the products of these reactions are cyclic or linear oligomers which, in some cases, consist of phosphazene rings or short chains linked through the alkyl side groups.

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Registry No. **3b**, 117896-80-7; **3d**, 117896-81-8; **3g**, 117896-82-9.

References and Notes

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