Macromolecules

Volume 23, Number 17 August 20, 1990

Synthesis of New Polyphosphazene Elastomers

Harry R. Allcock,* Gayann S. McDonnell, and James L. Desorcie

Department of Chemistry, The Pennsylvania State University, 152 Davey Laboratory, University Park, Pennsylvania 16802

Received February 7, 1990

ABSTRACT: The cyclic phosphazenes $N_3P_3F_5(CMe_3)$, $N_3P_3F_5Ph$, *non-gem*-$N_3P_3Cl_4Me_2$, *non-gem*-$N_3P_3Cl_4Et_2$, $(NPClMe)_3$, and $(NPClMe)_4$ have been polymerized to macromolecules of formula $[(NPF_2)_2\text{-}NPFR]_n$, $[NPCl_2(NPClR)_2]_n$, and $(NPClR)_n$. Species $(NPClMe)_3$ and $(NPClEt)_3$ were copolymerized with $(NPCl_2)_3$ to yield polymers of type $[(NPCl_2)_x(NPClR)_y]_n$. The halogen atoms in the high polymers were replaced by trifluoroethoxy groups to yield hydrolytically stable derivatives. The influence of the alkyl or aryl groups on the properties of the polymers is described. The new polymers are elastomers, with glass transition temperatures in the −40 to −60 °C range.

The main method for the synthesis of stable polyphosphazenes involves the polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to high molecular weight poly(dichlorophosphazene), $(NPCl_2)_n$, followed by replacement of the halogen atoms in this polymer by alkoxy, aryloxy, or amino groups.[1-4] In general, these polymers are microcrystalline materials if the side groups are OCH_2CF_3, OPh, or substituted phenoxy units and if only one type of side group is present along each chain. By contrast, polyphosphazenes with flexible side groups, such as OMe, OEt, or $OCH_2CH_2OCH_2CH_2OCH_3$, are elastomers. However, polymers that bear two or more different fluoroalkoxy or aryloxy side groups attached to the same chain are elastomers.[5-8] This is because the random distribution of different side groups along the chain prevents crystallization and allows the inherent flexibility of the polyphosphazene backbone to dominate the solid-state properties. Mixed-substituent fluoroalkoxyphosphazene polymers are used in technology as low-T_g solvent-, oil-, and oxidation-resistant elastomers.[5-8] Mixed-substituent (aryloxy)phosphazene elastomers are employed as nonburning, expanded foam insulation materials.

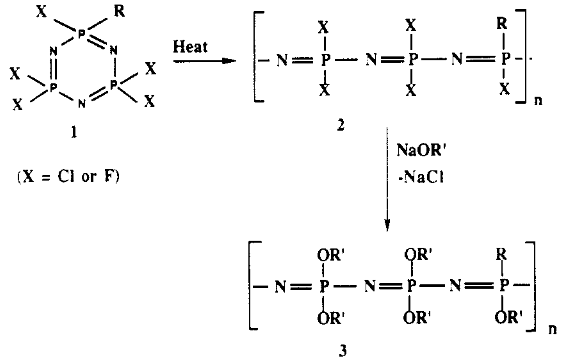
The work described in this paper is part of our program to synthesize a new class of phosphazene elastomers. This program is based on the following logic. If low-T_g elastomers can be prepared by the random introduction of two (ore more) different alkoxy or aryloxy groups into a polyphosphazene, it should be possible to generate other elastomers by the introduction of alkyl or aryl groups, together with alkoxy or aryloxy side units. Provided the difference in size of the two groups prevents crystallization and generates appreciable free volume, the generation of elastomeric properties is likely.

Two methods are available for testing this idea. First, poly(dichlorophosphazene) or poly(difluorophosphazene) might be allowed to react with an alkyl or aryl Grignard or organolithium reagent to replace some of the halogen atoms by alkyl or aryl groups. The remaining halogen atoms could then be replaced by alkoxy or aryloxy units. In earlier studies, we explored this method in some detail[9-12] but concluded that the approach is limited by the tendency of many organometallic reagents to cleave the skeletal bonds of $(NPCl_2)_n$. This is less of a problem when $(NPF_2)_n$ is used as a macromolecular substrate, but the large-scale synthesis of this polymer presents serious problems.[11]

The alternative approach has proved to be more useful. This involves the synthesis of phosphazene cyclic trimers or tetramers that bear both halogen and alkyl or aryl side groups (1). These are prepared by the reactions of $(NPCl_2)_3$ or $(NPF_2)_3$ with organometallic reagents, interactions that are less affected by skeletal cleavage processes than are the analogous reactions at the high polymeric level. Thermal polymerization of these alkyl- or arylhalogenocyclophosphazenes may yield linear or macrocyclic high polymers (2), the halogen atoms of which can then be replaced by alkoxy or aryloxy groups. This approach is summarized in Scheme I. Examples of the reaction sequence shown in Scheme I are known for systems in which R is Me, Et, *n*-Pr, *n*-Bu, Ph, carboranyl, or organosilicon units.[13-17] In principle, cyclic trimers that bear more than one alkyl or aryl group can be utilized in the same way. However, general synthesis routes to compounds of this type have become available only

0024-9297/90/2223-3873$02.50/0

Scheme I

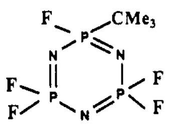


recently,[18,19] and relatively few examples have been studied as polymerization "monomers".

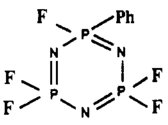
In this paper, we describe the polymerization of seven cyclophosphazenes. Two of these (**4** and **5**) correspond to structure **1**, with bulky R groups attached to the ring. The remaining five contain nongeminal halogeno–organo structures (**6**–**10**). In all cases, the polymers formed were subjected to reactions in which the halogen atoms were replaced by trifluoroethoxy groups to generate water stability. An analysis of the factors that facilitate or inhibit polymerization in these and related systems will be presented in a later publication.

Results and Discussion

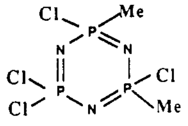
Cyclic Phosphazenes Used in This Work. The compounds shown as **4**–**10** were studied as "monomers" for polymerization. The polymerization of **5** was reported previously[13] but was included here as a control. Polymerization of **8** was mentioned briefly by Prons et al. in 1971,[20] but the polymer was apparently not converted to a stable derivative species. Analogues of **4** and **5** with methyl or ethyl groups in place of *tert*-butyl or phenyl, and chlorine in place of fluorine, have been polymerized in earlier studies.[14]



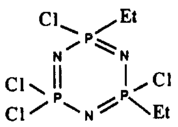
4



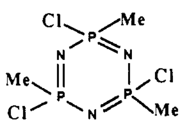
5



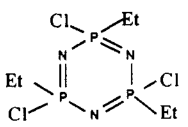
6



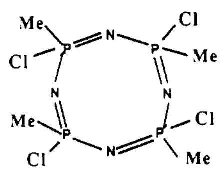
7



8



9



10

Species **4**–**10** were synthesized by the following methods. Compounds **4** and **5** were prepared by the organolithium method of Ramachandran and Allen[21] and Allen and Moeller.[22] Trimers **6**–**9** were prepared by the reactions of alkylmagnesium or alkylaluminum reagents with cyclotriphosphazenes that bear both dimethylamino and chloro side units.[18,19] The dimethylamino groups were then replaced by chlorine by reaction with hydrogen chloride. This strategy was also used to prepare the cyclic tetramer **10**.

Extensive efforts were made to ensure the purity of the cyclophosphazenes, since nearly all phosphazene polymerization reactions are sensitive to the presence of impurities. Vapor-phase chromatography, mass spectrometry, and NMR analysis were used to monitor the purity of each compound.

Polymerization and Substitution Reactions. Each compound was heated in evacuated sealed glass tubes at 210–250 °C (for the chlorophosphazenes) or 250–300 °C (for the fluoro derivatives). The best experimental conditions found are summarized in Table I. The polymers formed in this way are depicted by structures **11**–**15**. The same polymer, **15**, was formed from both **8** and **10** (Chart I). Polymers **16** and **17** were prepared by copolymerization of **8**, **9**, or **10** with $(NPCl_2)_3$.[23] These reactions took place at 250 °C with reaction times of 10–40 h, with the use of 1:1 molar ratios of $(NPClR)_{3\text{ or }4}$ and $(NPCl_2)_3$. As shown in Table I, $(NPClMe)_3$ (**8**) was preferentially incorporated into polymer **16**, compared to $(NPCl_2)_3$. Species $(NPClEt)_3$ appeared to have roughly the same reactivity as $(NPCl_2)_3$ since nearly equal amounts of the two species were incorporated into the copolymer.

The conditions needed for replacement of the halogen atoms in **11**–**17** by trifluoroethoxy groups were estimated by trial substitutions using cyclic species.[14,24] For example, it was found that compound **4** reacted with excess sodium trifluoroethoxide at 25 °C in tetrahydrofuran to replace only four of the five fluorine atoms. Only when the reaction was carried out at 65 °C was the fifth fluorine replaced.[25] This information was used to design the reaction conditions needed to replace the halogen atoms in **11**–**17** to yield polymers **18**–**24**.

Characterization and Properties of the Polymers. Ideally, a full characterization of the polymeric products should include a structural assessment of both the halogeno polymers **11**–**17** and their trifluoroethoxy derivatives **18**–**24**. In practice, it was found that the halogeno species were exceedingly sensitive to moisture and frequently cross-linked during attempted purification. For this reason, most of the characterization was carried out on the hydrolytically stable derivatives **18**–**24**, which could be prepared without isolation of their macromolecular precursors.

Nevertheless, some NMR characterization was possible for species **13**–**17** after swelling in THF and extractive removal of cyclic oligomers. For example, as shown in Table II, the ^{31}P NMR spectra of **13** (derived from **6**) and **16** (derived from **8** and $(NPCl_2)_3$) consisted of resonances at 10.7 (PClMe) and −22.8 ppm (PCl_2), while polymer **15** gave a resonance at 11.0 ppm only. The ^{31}P NMR spectra of **13**–**17** obtained in this way were consistent with the structures shown and with the side-group ratios of the derivative polymers **20**–**24**. Thus, replacement of the P–Cl (and presumably P–F) bonds by $P{-}OCH_2CF_3$ units appeared to bring about no detectable changes in the basic structures.

A more extensive characterization was possible for polymers **18**–**24**, and this involved a combination of ^{1}H and ^{31}P NMR spectroscopy, elemental analysis, infrared spectroscopy, differential scanning calorimetry (DSC), and gel permeation chromatography. Most of these data are summarized in Table II.

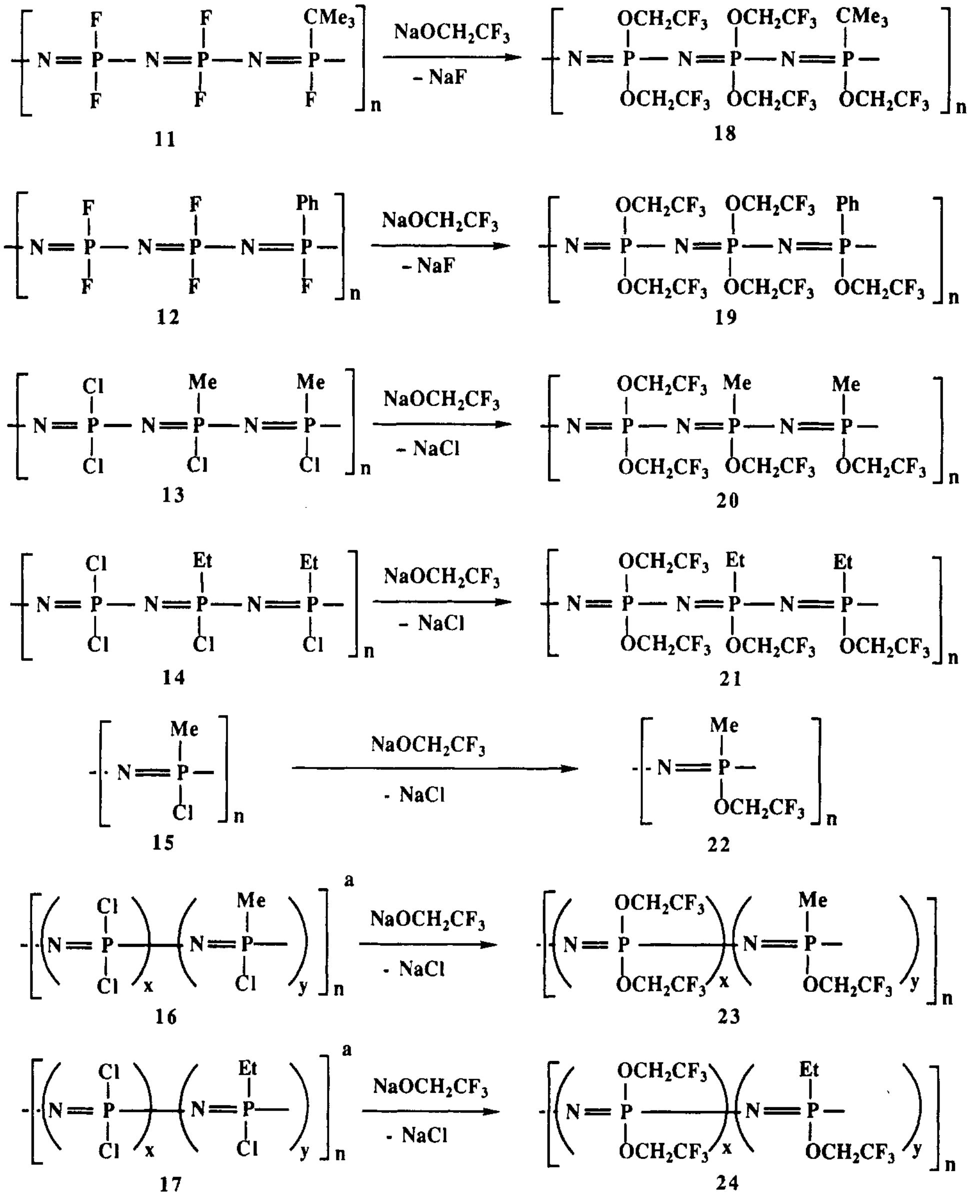
The infrared spectra of polyphosphazenes **18**–**24** were consistent with the proposed structures. In each case, an intense absorbance existed between 1100 and 1300 cm^{-1}.

Table I
Synthesis Data for Poly(organophosphazenes)

polymer	starting materials	temp, °C	time	yield,[a] %	% repeating units[b,c] NPR(OR′)	% repeating units[b,c] $NP(OR')_2$	molecular weight (×10⁻⁵) (GPC) M_w	molecular weight (×10⁻⁵) (GPC) M_n
18	**4**	300	4–6 days	49	35	65	4.6	1.1
19	**5**	300	2–3 days	59	33	67	12.0	1.3
20	**6**	250	6–50 h	46	65	35	5.1	0.87
21	**7**	250	6–50 h	42	64	36	2.8	0.28
22	**8**	250	4–20 h	31	100	0	7.0	2.4
22	**10**	250	30 h	25	100	0	6.6	1.8
23	**8** + $(NPCl_2)_3$[d]	250	10–40 h	44	61	39	8.9	1.7
24	**9** + $(NPCl_2)_3$[d]	250	10–40 h	48	53	47	6.7	0.66

[a] The products were ring-expansion/equilibration species. The polymer yields are for products isolated after replacement of halogen atoms in **11**–**17** by trifluoroethoxy groups. [b] Determined from ^1H, ^{31}P, and elemental microanalysis data. [c] OR′ = OCH_2CF_3. [d] Equimolar ratios.

Chart I



[a] Prepared by copolymerization of **8**, **9**, or **10** with $(NPCl_2)_3$.

This is a characteristic of the –P═N– skeleton in linear or macrocyclic polyphosphazenes. Other bands were detected for alkyl or aryl group C–H absorbances.

The ^{31}P NMR spectra for **18**–**24** are summarized in Table II. Although polymer **22** generated only a single sharp peak, the spectra of **18**–**21**, **23**, and **24** contained significantly broader resonances with considerable fine structure. This was attributed to a variety of microenvironments for the phosphorus atoms in the skeleton, perhaps complicated further by P–P spin–spin or through-space coupling. In any case, the broad resonances indicate that all the polymers except **22** possess a relatively random sequencing of repeating units. This was especially evident with polymers **20** and **21**. Polymers **15** and **22** yielded similar ^{31}P NMR spectra when prepared from either **8** or **10**. The use of **8** or **9** in copolymerization reactions with $(NPCl_2)_3$ provided different ratios of the two types of repeating units in **23** and **24**. These different structures

Table II
Polyphosphazene Characterization Data[a,b]

	^{31}P NMR,[c] ppm		^{1}H NMR, δ[c]			elemental microanalysis, %							
						found				calcd			
polymer	PRCl or PR(OR′)	PCl_2 or $P(OR')_2$	R	R′	T_g, °C	C	H	N	X	C	H	N	X
13[f]	10.7 (m)	−22.8 (m)											
14[f]	16.7 (m)	−22.2 (m)											
15[f]	11.0 (m)												
16[f]	10.8 (m)	−22.8 (m)											
17[f]	16.8 (m)	−21.8 (m)											
18	4.1 (m)	−9.5 (m)	1.24 (d)	4.50 (m)	−52	24.46	2.79	6.12	41.47[d]	24.45	2.81	6.39	39.38
19	4.5 (m)	−8.5 (m)	7.61 (m)	4.48 (m)	−46	27.17	2.14	5.94	39.70[d]	27.80	2.49	6.05	37.38
20	16.7 (m)	−8.3 (m)	1.72 (m)	4.48 (m)	−55	21.55	2.41	7.54	0.07[e]	21.63	2.62	7.75	
21	20.1 (m)	−8.9 (m)	2.01 (m)[g] 1.18 (m)[h]	4.51 (m)	−65	24.42	3.11	6.95	0.03[e]	24.87	3.18	7.25	
22	14.9 (s)		1.66 (d)[i]	4.43	−50	22.66	3.28	8.91	0.04[e]	22.64	31.4	8.81	
23	17.0 (m)	−8.2 (m)	1.70 (m)	4.50 (m)	−55 −44	21.25	2.48	7.38	0.05[e]	21.51	2.56	7.62	
24	20.9 (m)	−8.8 (m)	2.01 (m)[g] 1.19 (m)[h]	4.51 (m)	−64	23.31	2.70	6.73	0.05[e]	23.99	2.93	7.00	

[a] OR′ = OCH_2CF_3. [b] s = singlet, d = doublet, m = unresolved multiplet. [c] ^{31}P NMR spectra in THF solvent, ^{1}H spectra in acetone-d_6. [d] X = F. [e] X = Cl. [f] Polymer swelled in THF for NMR measurements, but did not dissolve. [g] CH_2 signal. [h] CH_3 signal. [i] J_{PH} = 14.0 Hz.

were detectable by ^{31}P NMR spectroscopy.

The structures of polymers **18–24** were also monitored by high-field ^{1}H NMR spectroscopy. These spectra were complicated by various proton–proton and proton–phosphorus coupling interactions. Peak integration techniques were used to determine the repeat unit ratios for polymers **23** and **24**. These were confirmed by microanalysis.

The glass transition temperatures (T_g) were measured for polymers **18–24** by DSC analysis. The results are shown in Table II. The T_g values can be compared with those of the single-substituent polymers $[NP(OCH_2CF_3)_2]_n$ (T_g = −66 °C) and $[NPMe_2]_n$ (T_g = −42 °C).[26] This comparison must be made with the recognition that both of these control polymers are microcrystalline materials, whereas the new polymers reported in this work are amorphous. The introduction of one ethyl group per two repeating units (**24**) affects the T_g hardly at all (−64 °C). Two separate glass transitions were detected for copolymer **23** (at −55 and −44 °C). This is surprising, but it may indicate that the polymer has some degree of block character. The T_g values of polymers **18** and **19**, with a bulky *tert*-butyl or phenyl side group every three repeating units, were slightly higher (−52 and −46 °C, respectively) than that of $[NP(OC_2CF_3)_2]_n$. Rigid bulky substituents probably raise the T_g by intramolecular steric interference to chain torsional motions.

None of the polymers **18–24** showed crystalline melting transitions in the DSC analyses. Moreover, the polymers generated no optical birefringence when viewed through crossed polarizers.

In the un-cross-linked state, polymers **18–24** are adhesive elastomers, with distinctly different properties from $[NP(OCH_2CF_3)_2]_n$ or $[NPMe_2]_n$. In addition, the methyl derivatives, **20**, **22**, and **23**, underwent slow viscous flow at room temperature. In many respects, polymers **18–24** resemble the commercial elastomers of formula $[NP(OCH_2CF_3)_x(OCH_2(CF_2)_mCF_2H)_y]_n$. Possible advantages over the established materials include the absence of side groups with potentially reactive terminal CF_2H units, a greater control over the substituent ratios, and the generation of low-T_g elastomeric properties without the use of high ratios of a second fluoroalkoxy side group.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was supplied by Ethyl Corp. Tetrahydrofuran (THF) was distilled into the reaction flask under an atmosphere of dry argon from a sodium benzophenone ketyl drying agent. Hexane was distilled from calcium hydride before use. Trifluoroethanol (Halocarbon Products) was distilled and then dried over 3-Å molecular sieves. Sodium stick (Aldrich) was stored, cut, and weighed in a nitrogen-filled drybox equipped with a recirculating atmosphere system to remove oxygen and water.

Analytical Equipment and Techniques. ^{31}P NMR spectra were recorded with the use of a JEOL FX-90Q spectrometer operated at 36 MHz. Positive chemical shifts are downfield from that of external phosphoric acid. ^{1}H NMR spectra were recorded with the use of a Bruker WP-200 spectrometer operated at 200 MHz. Chemical shifts are relative to tetramethylsilane at 0. Infrared spectra were recorded on a Perkin Elmer 283B spectrometer. The samples were prepared as thin films on NaCl disks. Vapor-phase chromatography was carried out by using a Varian 3700 gas chromatograph equipped with a flame ionization detector and a 2-m SP2100 (3%) column. Gel permeation chromatography (GPC) data were obtained with the use of a Hewlett-Packard HP 1090 liquid chromatograph with a refractive index detector. Polymer Laboratories PLgel (10^6, 10^6, and 10^3 Å) columns were calibrated with narrow molecular weight polystyrene standards. The columns had been previously calibrated with fractionated samples of $[NP(OCH_2CF_3)_2]_n$. A 0.1% solution of $(n\text{-}C_4H_9)_4NBr$ in THF was employed as the eluent. Glass transition temperatures (T_g) were recorded with the use of a Perkin-Elmer DSC-7 unit with a PE 7500 computer. The samples (10–30 mg) were analyzed in crimped aluminum pans: a heating rate of 10 °C/min and a helium flow rate of 10 mL/min were used. The instrument was calibrated with a cyclohexane standard with thermal transitions at −87.06 and 6.54 °C. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN.

Synthesis of Cyclic Trimers and Tetramer. Species **4–10** were synthesized by techniques described in the literature.[18,19,21,22] The cyclic tetramer **10** was obtained via the ring expansion reaction of **8** in an evacuated sealed tube at 210 °C for 6–25 days or at 250 °C from 4 h to 25 days. Yields of **10** varied from ~20% to 80% depending on reaction conditions. In general, the highest yields of **10** were associated with reactions at 250 °C for 1 day or longer. This and other cyclophosphazene equilibration reactions will be discussed in detail in another publication.

Compounds **4** and **5** were purified by vacuum distillation at 0.05 Torr. Cyclophosphazenes **6–10** and $(NPCl_2)_3$ were purified by two recrystallizations from dry hexane or heptane, followed by three vacuum sublimations at 0.05 Torr. The purified compounds were then stored in an inert-atmosphere drybox.

Polymerization Technique. The polymerizations were carried out in Pyrex glass tubes, 220 mm long, 12-mm o.d., and 10-mm i.d., with a constriction 100 mm from the open end. The tubes were soaked in ethanolic KOH for 24 h, followed by five washings each with tap water, 2% aqueous HCl solution, distilled water, and distilled/deionized water. They were then dried at 140 °C for 48 h. The tubes were charged with the appropriate cyclophosphazene (~3.0 g) in the drybox, attached to a vacuum line, and evacuated for 30 min at 0.05 Torr. The tubes were then sealed at the constriction, wrapped in aluminum gauze, and placed on a rocking device in a Freas thermoregulated oven preheated to the desired temperature. The viscosity of the molten reaction mixtures increased significantly as the contents of the tubes polymerized.

Model Reactions of 4 with $NaOCH_2CF_3$. Most of these reactions followed a similar set of procedures, and the following are typical.

$N_3P_3(OCH_2CF_3)_4F^tBu$. A solution of $NaOCH_2CF_3$, prepared from sodium (0.96 g, 0.04 mol) and $HOCH_2CF_3$ (3.5 mL, 0.048 mol) in THF (100 mL), was added dropwise to a solution of $N_3P_3F_5R$ (**4**) (2.0 g, 7.4 mmol) in THF (30 mL) which was cooled to −78 °C. The solution was warmed to room temperature and was neutralized with $ClSi(CH_3)_3$. The solution was added to distilled water (200 mL) and was then extracted with diethyl ether (3 × 150 mL). The ether layers were dried over magnesium sulfate and filtered, and the solvent was removed under reduced pressure. The product was purified by distillation: bp 96 °C, 0.05 Torr, yield 0.9 g, 21%; ^{31}P NMR 14.4 ppm (d) ($P(OCH_2CF_3)_2$), 52.5 ppm (d, t) (PF^tBu, $J_{PNP} = 39.1$ Hz, $J_{PF} = 1025.4$ Hz); ^1H NMR δ 1.2 (d) (^tBu), 4.2 (m) (OCH_2CF_3, $J_{PH} = 19.1$ Hz); IR (oil) ν_{CH} 2980 cm^{-1}, ν_{PN} 1180, 1260, 1300 cm^{-1}. Anal. Calcd for $C_{21}H_{17}N_3P_3O_4F_{13}$: C, 23.73; H, 2.83; N, 6.29; F, 40.68. Found: C, 23.90; H, 2.83; N, 6.89; F, 41.17.

Synthesis of $N_3P_3(OCH_2CF_3)_5{}^tBu$. Compound **4**, $N_3P_3F_5{}^tBu$ (2.0 g, 7.41 mmol), dissolved in THF (30 mL) was added to a refluxing solution of $NaOCH_2CF_3$ prepared from sodium (2.4 g, 0.10 mol) and $HOCH_2CF_3$ (9.0 mL, 0.124 mol) in THF (100 mL). The solution was refluxed for 8 days. The product was isolated as described above: yield 1.2 g, 30%; mp 38 °C; ^{31}P NMR (AX_2) ν_A 49.0 ppm ($P(OCH_2CF_3){}^tBu$), ν_X 16.9 ppm ($P(OCH_2CF_3)_2$, J_{PNP} = 39.1 Hz); ^1H NMR δ 4.2 (m) (OCH_2CF_3), 1.2 (d) (^tBu, J_{PH} = 18.7 Hz); IR (KBr) ν_{CH} 2945 cm^{-1}, ν_{PN} 1165, 1240, 1280 cm^{-1}. Anal. Calcd for $C_{14}H_{19}N_{33}O_5F_{15}$: C, 24.47; H, 2.79; N, 6.12; F, 41.48. Found: C, 24.49; H, 2.75; N, 6.13; F, 41.53.

Reactions of Polymers 11–17 with $NaOCH_2CF_3$. All these reactions were carried out in a similar manner. The following procedure is typical. A polymerization tube containing a mixture of **15** and cyclic oligomers (3.0 g, 0.031 mol) was opened in a nitrogen-filled glovebag, and the contents were dissolved in dry THF (100 mL). A solution of $NaOCH_2CF_3$ in THF (25 mL) was prepared from sodium (1.5 g, 0.065 mol) and trifluoroethanol (8.9 g, 0.089 mol) under an atmosphere of dry argon. The solution of **15** was added to the $NaOCH_2CF_3$ at 25 °C over a period of 30 min. The reaction mixture was then heated to reflux for 8 h. The mixture was allowed to cool to room temperature, and chlorotrimethylsilane (7.3 g, 0.067 mol) was added to destroy unreacted $NaOCH_2CF_3$. The reaction mixture was stirred for 2 h, and the solvent was removed under reduced pressure. The residue was then Soxhlet-extracted with pentane for 48 h to remove cyclic oligomers. The polymer (**22**) was dissolved in acetone (20 mL) and was isolated following precipitation into water. The product was further purified by two reprecipitations from acetone into water followed by two reprecipitations from acetone into pentane. The polymer was dried for 48 h in vacuo.

Examination of Chloro-Substituted Phosphazenes 13–17. Each polymerization tube was opened in a nitrogen-filled glovebag, and the contents were Soxhlet-extracted with dry hexane for 48 h. The recovered polymers would not dissolve in THF, but they swelled sufficiently to allow ^{31}P NMR spectra to be recorded. Acceptable ^{31}P NMR spectra of **11** and **12** were not obtainable because of their limited solubility and the extensive P–F coupling interactions.

Acknowledgment. We thank the U.S. Office of Naval Research for the support of this work.

References and Notes

(1) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(2) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(3) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.
(4) Allcock, H. R. *ACS. Symp. Ser.* **1988**, *360*, 250.
(5) Rose, S. H. *J. Polym. Sci. B* **1968**, *6*, 837.
(6) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33.
(7) Singler, R. E.; Hagnauer, G. L.; Sicka, R. W. *ACS Symp. Ser.* **1982**, *193*, 229.
(8) Penton, H. R. *ACS Symp. Ser.* **1988**, *360*, 277.
(9) Allcock, H. R.; Chu, C. T.-W. *Macromolecules* **1979**, *12*, 551.
(10) Allcock, H. R.; Evans, T. L.; Patterson, D. B. *Macromolecules* **1980**, *13*, 201.
(11) Evans, T. L.; Allcock, H. R. *J. Macromol. Sci., Chem.* **1981**, *A16* (1), 409.
(12) Evans, T. L.; Patterson, D. B.; Suszko, P. R.; Allcock, H. R. *Macromolecules* **1981**, *14*, 218.
(13) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.
(14) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules* **1980**, *13*, 1332.
(15) Allcock, H. R.; Connolly, M. S. *Macromolecules* **1985**, *18*, 1330.
(16) Allcock, H. R.; Scopelianos, A. G.; O'Brien, J. P.; Bernheim, M. Y. *J. Am. Chem. Soc.* **1981**, *103*, 350.
(17) Allcock, H. R.; Brennan, D. J.; Graaskamp, J. M. *Macromolecules* **1988**, *21*, 1.
(18) Allcock, H. R.; Desorcie, J. L.; Rutt, J. S. *Organometallics* **1988**, *7*, 612.
(19) Allcock, H. R.; Desorcie, J. L.; Wagner, L. J. *Inorg. Chem.* **1985**, *24*, 333.
(20) Prons, V. N.; Grinblat, M. P.; Klevanskii, A. L. *Zh. Obshch. Khim.* **1971**, *41*, 482.
(21) Ramachandran, K.; Allen, C. W. *J. Am. Chem. Soc.* **1982**, *104*, 2396.
(22) Allen, C. W.; Moeller, T. *Inorg. Chem.* **1968**, *7*, 2177.
(23) No high polymer was formed from trimer **9** alone. Instead, a series of higher cyclic oligomers was generated. This ring-expansion process, and its relationship to high polymer formation, will be discussed in a later paper.
(24) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(25) The characterization data for $N_3P_3(OCH_2CF_3)_5CMe_3$ (derived from **4**) differed from that of a compound prepared previously from $N_3P_3Cl_5CMe_3$.[14] A repeat of that earlier synthesis indicated that the earlier data corresponded to *gem*- $N_3P_3Cl(OCH_2CF_3)_4CMe_3$. Only under forcing conditions was the final chlorine atom replaced. This, too, was an indication of the low reactivity of a halogen atom geminal to a *tert*-butyl group, presumably a consequence of steric shielding.
(26) Polymers of this structure have been prepared by a condensation route from *P*-(trifluoroethoxy)-*N*-silylphosphinimines: Neilson, R. H.; Hani, R.; Wisian-Neilson, P.; Meister, J. J.; Roy, A. K.; Hagnauer, G. L. *Macromolecules* **1987**, *20*, 910.

Registry No. **4**, 81095-56-9; **4** (homopolymer), 128135-73-9; **5** (homopolymer), 56636-14-7; **6** (homopolymer), 128135-74-0; **7** (homopolymer), 128135-75-1; **8** (homopolymer), 128135-76-2; (**8**)-$(NPCl_2)_3$ (copolymer), 84515-99-1; (**9**)$(NPCl_2)_3$ (copolymer), 128135-78-4; **10**, 128135-77-3; **15**, 83592-05-6; $NaOCH_2CF_3$, 420-87-1; $N_3P_3(OCH_2CF_3)_5Bu$-*t*, 75155-12-3.