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(5) T_1 measurements were carried out at the elevated temperatures to determine a proper selection of repetition times and pulse widths for quantitative results. Because of an accompanying reduction in molecular weight, i.e., viscosity, as the thermolysis of the polymer proceeded, T_1 measurements were made in the latter stages of rearrangement when the T_1 values would be the highest. Nuclear Overhauser Enhancement (NOE) measurements were made on the polymer peaks and were within 4% of each other. Consequently, the integral values for the polymer peaks should be quite quantitative. NOE measurements were not made on the cyclic tetramer.

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A New Route for Poly(organophosphazene) Synthesis. Polymerization, Copolymerization, and Ring–Ring Equilibration of Trifluoroethoxy- and Chloro-Substituted Cyclotriphosphazenes[1,2]

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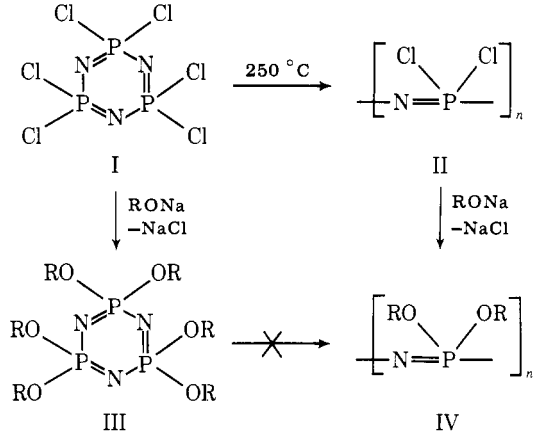
ABSTRACT: The phosphazene cyclic trimer, $[NP(OCH_2CF_3)_2]_3$ (X), copolymerizes with $(NPCl_2)_3$ (I) to yield a new series of elastomers and also undergoes ring-expansion reactions at elevated temperatures. The copolymers were characterized by means of substitution reactions and ^{31}P NMR analysis. The possibility that the polymerization involves a prior ligand exchange was investigated through studies of the thermal behavior of the cyclic phosphazenes, $N_3P_3Cl_5(OCH_2CF_3)$ (V), $N_3P_3Cl_4(OCH_2CF_3)_2$ (trans nongem) (VI), $N_3P_3Cl_3(OCH_2CF_3)_3$ (trans nongem) (VII), $N_3P_3Cl_2(OCH_2CF_3)_4$ (cis nongem) (VIII), and $N_3P_3Cl(OCH_2CF_3)_5$ (IX). All these mixed substituent trimers underwent ring expansion reactions when heated, but only compounds V, VI, and VII yielded linear-type polymers. The gas, CF_3CH_2Cl, was detected as a product from all systems that contained both P–Cl and P–OCH_2CF_3 bonds, with substantial quantities being released at temperatures above 250 °C. This process was apparently connected with the formation of trans-annular-linked cyclic compounds, cross-linked linear chains, or cyclolinear or cyclomatrix-type products. The mechanisms of these reactions are discussed.

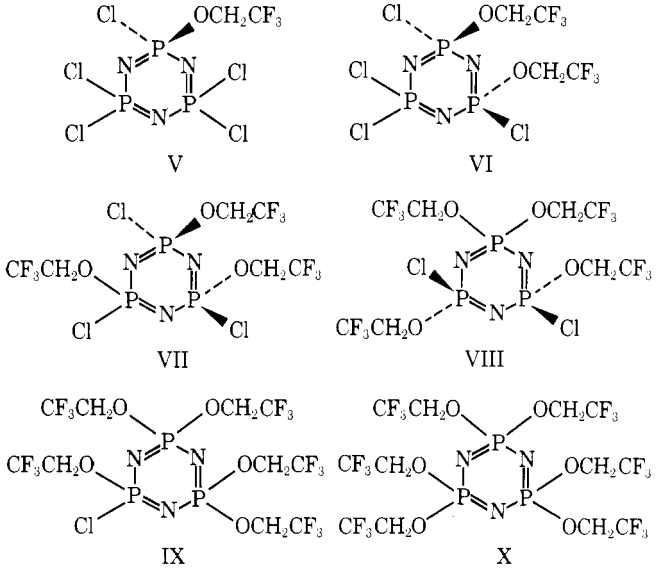
Hexachlorocyclotriphosphazene (I) can be polymerized thermally at temperatures above 230 °C to yield the rubbery, hydrolytically labile poly(dichlorophosphazene) (II). Allcock, Kugel, and Valan[3–5] first showed that a broad range of hydrolytically stable and technologically useful polymers can be prepared from II by treatment with nucleophiles such as alkoxides, aryloxides, or amines, and this synthetic route has been widely developed in a number of laboratories.[6–12] The alternative route to the synthesis of poly(organophosphazenes) (IV) via the direct polymerization of hexa(organo)cyclotriphosphazenes (III) has met with little success.



I II III IV

Earlier, we reported the polymerization of cyclotriphosphazenes that contain both phenyl and chloro groups.[13] That work suggested that phosphorus–halogen bonds were necessary before polymerization would occur. Thus, the possibility was foreseen that hexaorgano-substituted cyclotriphosphazenes, such as III, might copolymerize with halogen-containing species, such as I.

To test this hypothesis, copolymerizations were attempted between hexakis(trifluoroethoxy)cyclotriphosphazene (X) and hexachlorocyclotriphosphazene (I). Moreover, compounds V–IX had recently been isolated and characterized in our laboratory,[14] and it was of interest to examine the variation of polymerizability with increasing trifluoroethoxy substitution and the possibility that species, such as V–IX, might be formed as polymerization intermediates when X reacts with I.



V VI VII VIII IX X

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Table I
Copolymerization and Ring-Expansion Reactions between $(NPCl_2)_3$ (I) and $[NP(OCH_2CF_3)_2]_3$ (X) [a]

Mol of I ($\times 10^{-3}$)	Mol of X ($\times 10^{-3}$)	Molar ratio I:X	Reaction time, [b] days	Mol of CF_3CH_2Cl ($\times 10^{-5}$)	$[NP(OCH_2CF_3)_2]_n$ [c] cyclic oligomers, %, n = 3	4	5	6	$(NPCl_2)_n$ [c] cyclic oligomers, %, n = 3	4	Polymeric products
	3.42	0:100	42		98	1.5	Trace	Trace			
0.025	2.47	1:99	42		56	37	5	1			
0.25	2.25	10:90	42	3.7	13	52	11	*f*	1	*f*	
1.25	3.75	25:75	5.9	18.0	44	56	3				
5.00	5.00	50:50	2.4	8.7	+				+		*g*
7.50	2.50	75:25	3.9	2.9	+				+		*h*
9.00	1.00	90:10	4.2	0.97	9				70		~22% $(NPCl_2)_n$ [e]
9.90	0.10	99:1	42						99	1	Trace
8.62		100:0	42						99	1	Trace

[a] At 200 °C. [b] Time required to reach immobilization of the mixture at 200 °C (except for the 0:100, 1:99, 10:90, 99:1, and 100:0 molar mixtures which were still fluid when the reaction times were terminated). [c] A plus sign means that the compound was detected but its relative concentration was not measured. [d] Based on ^{31}P NMR analysis. [e] No $NP(OCH_2CF_3)_2$ residues could be detected by ^{31}P NMR analysis. [f] The remaining 16% of the total product formed three additional peaks (3, 12, and 1%) in the VPC plot. These species could not be identified unambiguously by VPC–mass spectral techniques. They are presumed to be ligand-exchanged or monomer residue-exchanged products. [g] Polymer containing ~50% $NPCl_2$ and 50% $NP(OCH_2CF_3)_2$ units (footnote *d*). [h] Polymer containing ~72% $NPCl_2$ and 12% $NP(OCH_2CF_3)_2$ units.[d]

Results

Copolymerization of X with I. General Features. The cyclic trimers $[NP(OCH_2CF_3)_2]_3$ (X) and $(NPCl_2)_3$ (I) reacted at elevated temperatures to yield a variety of products. The course of the reaction was markedly dependent on the temperature. At 200 °C mixtures that contained from 10 mol % through 50 mol % of X in I yielded colorless, elastomeric copolymers of formula $[NPCl_x(OCH_2CF_3)_y]_n$ (Table I). For example, mixtures that contained 50 mol % of X and I initially yielded a colorless, transparent, mobile melt at 200 °C. After 25–30 h at this temperature the liquid became viscous and then totally immobile after about 32–33 h. When cooled to 25 °C, the immobile polymers were hydrolytically unstable, rubbery elastomers that swelled greatly in benzene but did not dissolve. Soluble polymers were obtained during the critical reaction stage that preceded immobilization at 200 °C.

The copolymerization reactions at 200 °C were examined from two points of view. First, the structures of the polymers were examined by ^{31}P NMR techniques and by characterization of hydrolytically stable substituted products. Second, the influence of the reactant ratios and the polymerization time (at constant 1:1 ratio) were studied at 200 °C in an attempt to elucidate the polymerization mechanism. These approaches are examined in the following sections.

At temperatures above 200 °C, mixtures containing from 6 mol % through 95 mol % of X in I in evacuated sealed tubes exploded from internal gas pressure build-up. The gas was identified as CF_3CH_2Cl by mass spectrometry. This process will be discussed in a later section.

Structure of the Polymers. The formation of polymers by the interaction of I and X raised the following questions about the structure of the products. Does the reaction yield one or two homopolymers? If the products are copolymers, are they genuine linear copolymers, cyclolinear copolymers (perhaps with linear $(NPCl_2)_n$ segments linking $[NP(OCH_2CF_3)_2]_3$-based bridging groups), or graft copolymers in which cyclic trifluoroethoxyphosphazene trimer residues or linear species are grafted onto an $(NPCl_2)_n$ main chain? If the copolymer is essentially linear, do two chloro or trifluoroethoxy groups remain attached to each phosphorus, or does *ligand* scrambling occur? Do the $(NPCl_2)_3$ and $[NP(OCH_2CF_3)_2]_3$ units enter the polymer as trimer blocks, or does *monomer* unit scrambling take place? Finally, are cross-links formed and, if so, what is their chemical composition? Many of these questions are answered by the present work.

The composition of a representative copolymer was first determined by microanalysis and by ^{31}P NMR data. This composition was then confirmed by substitution techniques. The interaction of a 1:1 molar mixture of X and I at 200 °C yielded a hydrolytically unstable elastomer that was found by microanalysis to contain approximately 40–55% of the side groups as trifluoroethoxy residues and 45–60% as chlorine. ^{31}P NMR spectra of a number of polymers prepared under similar conditions suggested a composition with 40–48% OCH_2CF_3 and 52–60% as chlorine.

This general composition was confirmed by reaction of the copolymer with piperidine to yield a hydrolytically stable derivative of formula $[NP(NC_5H_{10})_x(OCH_2CF_3)_y]_n$. This was shown by microanalysis to contain approximately 40–45% of trifluoroethoxy and 55–60% of piperidino groups. The infrared spectrum (see Experimental Section) of this polymer was indicative of an open chain polymeric structure.

Treatment of the same $[NP(Cl)_x(OCH_2CF_3)_y]_n$ copolymer with sodium trifluoroethoxide yielded a polymer of composition $[NP(OCH_2CF_3)_2]_n$. The ^{31}P NMR spectrum of this product was identical to that of an authentic sample of open chain $[NP(OCH_2CF_3)_2]_n$ prepared from II.[3,4]

The open-chain structure of the $[NP(Cl)_x(OCH_2CF_3)_y]_n$ copolymer (i.e., the noncyclolinear structure) was also indicated by ^{31}P NMR analysis of this material. A typical spectrum is reproduced in Figure 1. The cyclic trimers $[NP(OCH_2CF_3)_2]_3$ (X) and $(NPCl_2)_3$ (I) show chemical shifts (relative to H_3PO_4) of +16.5 ± 0.2[15] and +19.4 ± 0.1 ppm, respectively. However, the copolymer showed chemical shifts at −8.3, −9.4, −10.8, and −18.8 ppm. Open-chain high-polymeric $[NP(OCH_2CF_3)_2]_n$ shows a shift of −8.4 ppm, and high-polymeric $(NPCl_2)_n$ has a chemical shift of −18.8 ppm. Negative ^{31}P chemical shifts are usually seen for linear phosphazene high polymers, whereas positive shifts are characteristic of cyclic trimers. Cross-linked samples of $[NP(Cl)_x(OCH_2CF_3)_y]_n$ that had been swelled in benzene and extracted with the same solvent showed no positive ^{31}P shift peaks, although unextracted materials showed peaks that indicated the presence of unreacted $[NP(OCH_2CF_3)_2]_3$. Hence, the polymers do not contain either $(NPCl_2)_3$ or

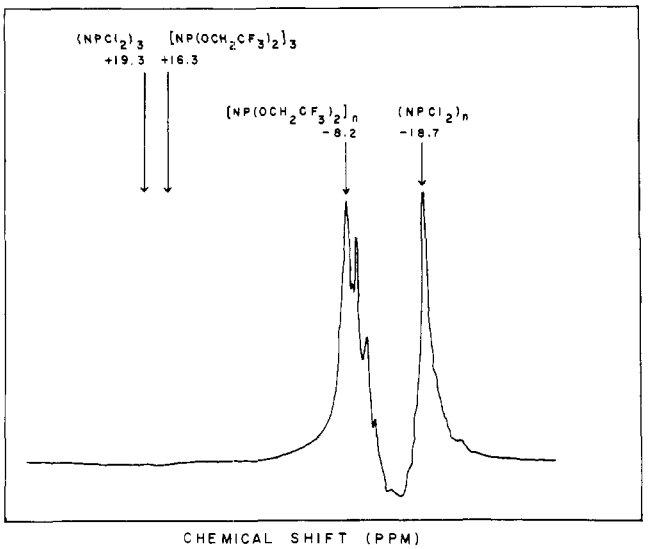


Figure 1. ^{31}P NMR spectrum of a lightly cross-linked form of the copolymer, $[NPCl(OCH_2CF_3)]_n$, prepared by the interaction of an equimolar mixture of $(NPCl_2)_3$ and $[NP(OCH_2CF_3)_2]_3$ at 200 °C for 50 h. The spectrum was obtained for a swollen gel in benzene. See ref 15 for the sign convention.

$[NP(OCH_2CF_3)_2]_3$ cyclic residues covalently grafted onto the main chain.

With the open-chain structure established, the question remained of whether the polymer contained short or long homopolymer blocks or ligand-exchanged species. ^{31}P NMR spectra are, in principle, capable of distinguishing between the 18 triad sequences made up of the various combinations of the repeating units $NPCl_2$ (A), $NPCl(OCH_2CF_3)$ (B), and $NP(OCH_2CF_3)_2$ (C). The existence of ^{31}P shifts for the polymer at −18.7 ppm strongly suggested the presence of sequences of type AAA in appreciable concentrations. Moreover, the presence of a peak at −8.2 ppm was consistent with triads of type CCC. The peaks at −9.4 and −10.8 ppm are shifted so little from the peak at −8.2 ppm that it seems reasonable to assign them to sequences such as ACA, ACC, BCA, BCB, or BCC, rather than to structures such as ABA, ABC, CBC, BBA, BBB, or BBC. These latter structures would be expected to yield shifts in the region of −15 ppm if the behavior of the cyclic analogues can be extrapolated to the polymer.[14] Thus, although some structural ambiguity remains, the ^{31}P NMR results suggest that ligand exchanged repeating units do not comprise a high proportion of the units in the polymer structure.

The present results provide little information about the presence of linear branches or cross-links. Light cross-linking is assumed to be responsible for the insolubility but swellability of some of the polymers. Indeed, the degree of solvent absorption by the polymer decreases as the polymerization time is increased and the extensibility of the elastomer is correspondingly reduced. This behavior is fully consistent with the existence of cross-links, although their concentrations in the polymers studied were too low to be evident in ^{31}P NMR or infrared spectra. A plausible mechanism for cross-linking involves intermolecular elimination of CF_3CH_2Cl with the concurrent formation of P–O–P cross-links. This aspect is discussed in a later section.

Mechanistic Factors. The polymerization of pure $(NPCl_2)_3$ (I) is very slow at temperatures below 230 °C, and pure $[NP(OCH_2CF_3)_2]_3$ (X) yields no polymer when heated at temperatures up to 300 °C. Thus, the mechanism of formation of copolymers from these two species at 200 °C is a subject of some fundamental interest.

Table II
Copolymerization of I with X [a,b]

Reaction time, h	Product ratio I:X[c]	Product ratio (I + X):other cyclic species[d]	Polymer composition $[NPCl_2]_n$:$[NP(OCH_2CF_3)_2]_n$[e]	Appearance
1	1:1			*g*
2	1:1			*g*
8	1:1.4			*g*
12	1:1.6	1:0.005		*g*
24	1:1.3	1:0.024		*g*
27	1:1.5	1:0.025	1:1.3	*g*
30	1:1.7	1:0.041	1:0.8	*h*
32	1:2.0	1:0.055	1:0.9	*i*
36	1:2.1[f]	1:0.13	1:0.9	*i*
50	1:2.4[f]	1:0.16	1:1.0	*i*

[a] The initial molar ratio of I:X was 1:1. [b] At 200 °C. [c] Values listed are ratios derived from VPC analysis. [d] From VPC analysis. [e] Including sequences attributed to ACA and ACC sequences, etc. (from ^{31}P NMR data). [f] Trimers extracted from polymer gel. [g] Mobile liquid at 200 °C; crystalline conglomerate at 25 °C. [h] Some melt viscosity observed at 200 °C. [i] Immobile at 200 °C; elastomer at 25 °C.

The following mechanistic questions need to be answered. First, does I function as an accelerator for the polymerization of X, or does X act as an accelerator for the polymerization of I? Second, do variations in the ratio of X and I alter the ratio of the two substituent groups in the polymer? Third, does X function as a chain terminator for the polymerization of I? Fourth, even though the copolymer made from an equimolar mixture of X and I contains roughly equal amounts of CF_3CH_2O and Cl side groups, are both starting materials consumed at the same rate? Fifth, does the copolymerization involve the interaction of X and I only, or do these two species interact to form reactive intermediates that are responsible for the polymerization? If so, what are the structures of the intermediates?

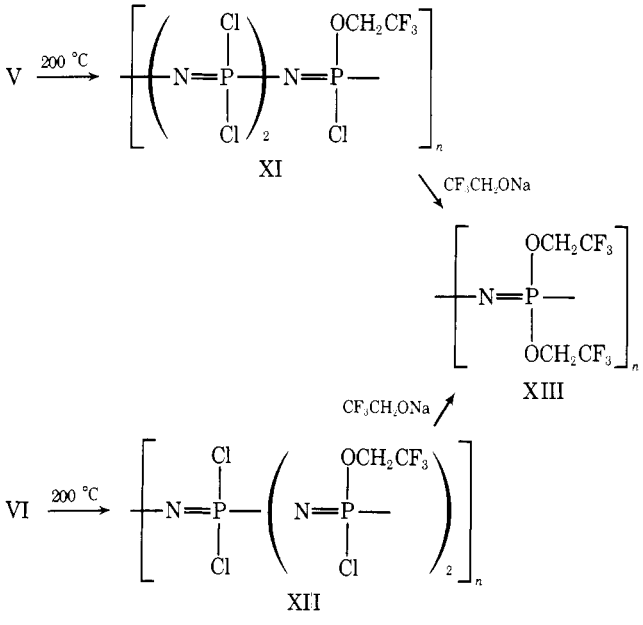
Table I summarizes the results of variations in the reactant ratios. Small amounts of X served to accelerate the polymerization of I at 200 °C, but small amounts of I did not induce the polymerization of X. However, I appears to accelerate the ring expansion reactions of X, and this aspect is discussed in a later section. As might be expected, a reduction in the amount of X relative to I in the copolymerization mixture reduced the relative proportion of trifluoroethoxy group in the copolymer (Table I). When the reactant ratio of I:X was reduced to 9:1, the polymeric product formed was virtually pure $(NPCl_2)_n$ (II). Although X permits the polymerization of I at a lower temperature than is normally required for the polymerization alone, the molecular weights of the copolymers are lower than those of polymers prepared from I alone (at 250 °C). Thus, the copolymerization of a 1:1 molar mixture of X and I at 200 °C, followed by reaction with sodium trifluoroethoxide, yielded a polymer of composition $[NP(OCH_2CF_3)_2]_n$, with an $\overline{M}_n$ value near 110 000. The same polymer prepared directly from $(NPCl_2)_n$ had an $\overline{M}_n$ of >500 000. Clearly, because of the ratios of CF_3CH_2O to Cl side groups in the polymer, X does not function as an efficient chain terminator. However, the evidence suggests that its copolymerization *reactivity* is lower than that of I.

This was confirmed by a ^{31}P NMR and vapor phase chromatography analysis of the reaction mixtures before gelation occurred (Table II). At 200 °C, starting from a 1:1 molar mixture of I and X, the concentration of I fell at a faster rate than did the concentration of X almost from the start of the reaction. After 8 h of reaction, the ratio of I:X was 1:1.4. Im-

mediately before gelation of the copolymer (~30 h) the ratio of residual I:X was 1:1.5; after gelation this ratio changed to 1:2.0.

The possibility that the polymerization of I with X proceeded through the intermediate formation of ligand-exchanged or ring-expanded species was evaluated by examination of the reaction mixtures by ^{31}P NMR spectroscopy, vapor phase chromatography (VPC), and VPC–mass spectrometry. The results are included in Table II. Both VPC and VPC–mass spectrometry data indicated the formation of low concentrations of new low molecular weight species after 8–9 h of reaction at 200 °C. These compounds slowly increased in concentration as the reaction proceeded. They were identified as $N_3P_3Cl_2(OCH_2CF_3)_4$, $N_4P_4Cl_3(OCH_2CF_3)_5$, and $N_4P_4Cl_4(OCH_2CF_3)_4$. The results suggest that *both* ligand-exchange and ring-enlargement reactions occur either as preliminary steps to polymerization or as noncontributing side reactions. This observation clearly raised the question of whether or not mixed substituent trifluoroethoxy–chlorophosphazene cyclic trimers were capable of thermal polymerization, and this aspect is discussed in the following section.

Polymerization Behavior of V–IX. The mixed substitutent trimers, V–IX, were synthesized by the reactions of sodium trifluoroethoxide with I.[14] At 200 °C, compounds V and VI polymerized during 48 h to yield the colorless, elastomeric polymers XI and XII. The other trimers were unreactive at this temperature. Polymers XI and XII were treated with sodium trifluoroethoxide to yield poly[bis(trifluoroethoxy)-phosphazene] (XIII), a known polymer that was prepared and fully characterized in earlier work.[3,4]



Polymers XI and XII were hydrolytically unstable. Hence, their structures were inferred indirectly from the structure of the hydrolytically stable XIII. First, the elemental composition, physical properties, and appearance of XIII closely resembled those of high polymeric $[NP(OCH_2CF_3)_2]_n$ obtained directly by the treatment of II with sodium trifluoroethoxide.[3,4,12] Second, the ^{31}P NMR spectrum of XIII showed a single peak at −8.3 ppm (upfield) relative to 85% H_3PO_4. This is comparable to the −8.4 ppm value found for authentic samples of $[NP(OCH_2CF_3)_2]_n$ but differs markedly from the +16.3-ppm value recorded for $[NP(OCH_2CF_3)_2]_3$.[14,15] Third, the thermal depolymerization of XIII at 400 °C in a helium flow tube system yielded the same cyclic oligomeric products in the same ratios as were observed previously from the depolymerization of open-chain $[NP(OCH_2CF_3)_2]_n$.[16] Thus, the evidence indicates that XIII is indeed $[NP(OCH_2CF_3)_2]_n$ and that this product was formed from polymers of structure XI and XII. This evidence was considered to be sufficient to rule out the possibility that XI and XII were cyclolinear polymers formed by the linkage of intact trimeric rings. However, polymer XIII was of lower molecular weight ($\bar{M}_n$ range 100 000–400 000 by gel permeation chromatography) than $[NP(OCH_2CF_3)_2]_n$ prepared from II ($\bar{M}_n$ range typically from 500 000 to over 3×10^6).

Table III
Ring-Expansion Reactions of $[NP(OCH_2CF_3)_2]_3$ (X)[a]

Initial system	Reaction time, h	$[NP(OCH_2CF_3)_2]_3$	$[NP(OCH_2CF_3)_2]_4$	$[NP(OCH_2CF_3)_2]_5$
X + IX (9:1 ratio)[c]	92	18	74	3
X + IX (99:1 ratio)	92	59	37	4
X + IX (999:1 ratio)	92	83	15	2[d]
X + CsCl (9:1 ratio)	92	66	32	3
X + CsCl (999:1 ratio)	92	84	14	2[d]
X	46	92	8	1
X	92	85	13	2[d]
X	184	67	29	3[d]
$[NP(OCH_2CF_3)_2]_4$	92	21	74	4

[a] All reactions were carried out at 275 °C. [b] The yields of the products are in mol %. [c] The products from this equilibration also included about 4 mol % $N_4P_4Cl(OCH_2CF_3)_7$ and traces of $N_5P_5Cl(OCH_2CF_3)_9$, as well as a trace of IX. [d] A trace of $[NP(OCH_2CF_3)_2]_6$ was also present.

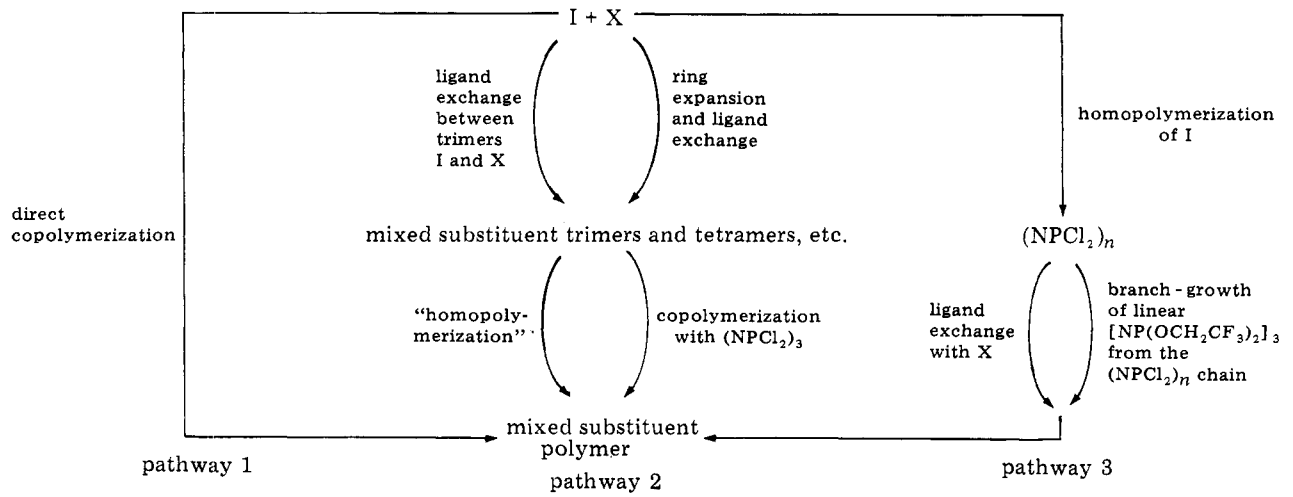
Compound VII polymerized at 225 °C (but not at 200 °C) during 48 h to yield a chlorotrifluoroethoxyphosphazene polymer which, when treated with sodium trifluoroethoxide, formed XIII. However, compounds VIII, IX, and X yielded no open-chain polymers when heated at temperatures up to 275 or 300 °C.

Ring–Ring Equilibrations. Compound X was found to undergo ring-expansion reactions at 275 °C to yield the cyclic tetramer, pentamer, and hexamer. This occurred slowly in the absence of any initiator but more rapidly in the presence of cesium chloride or $N_3P_3Cl(OCH_2CF_3)_5$ (IX) (Table III). Moreover, at 200 °C, ring-expansion reactions occurred in the presence of up to 25% of I, with the reaction apparently being accelerated by larger amounts of I. However, this ring expansion is a very slow process. The results in Tables I and III suggest that the reaction is a genuine equilibration although equilibrium is apparently not reached even after 42 days at 200 °C in the absence of $(NPCl_2)_3$. The surprising fact is that pure X undergoes a ring-expansion reaction at all in the view of its resistance to polymerization, and the implications of this are discussed in a later section.

Compounds VII–IX were also found to undergo ring–ring interconversion reactions at elevated temperatures.[17] For example, compound IX yielded the following products[18] when heated at 250 °C for 48 h (parent mass spectral peaks are given in parentheses): $N_4P_4(OCH_2CF_3)_8$ (972),[19] $N_4P_4Cl(OCH_2CF_3)_7$ (908 doublet), $N_4P_4Cl_2(OCH_2CF_3)_6$ (844), $N_4P_4Cl_3(OCH_2CF_3)_5$ (780), $N_5P_5Cl_2(OCH_2CF_3)_8$ (1087),[19] and $N_5P_5Cl_3(OCH_2CF_3)_7$ (1023). Higher cyclic species were also presumably formed, but these were beyond the range of detection of the mass spectrometer. The products formed from VIII after heating at 200 °C for 48 h included compounds such as $N_4P_4Cl_3(OCH_2CF_3)_5$ and species apparently formed by the elimination of CF_3CH_2Cl from $N_4P_4Cl(OCH_2CF_3)_7$. Thus, the evidence suggests that ring–ring interconversions are accompanied by side-group exchange reactions.

Decomposition Products. Three additional types of

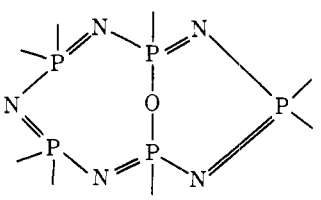
Scheme I
Possible Pathways for the Copolymerization of $(NPCl_2)_3$ (I) and $[NP(OCH_2CF_3)_2]_3$



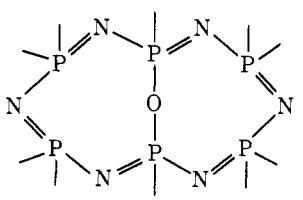
products were identified from the thermal reactions of V–IX. These included gaseous CF_3CH_2Cl, an infusible pyrolysis residue, and cyclic pyrolysis species. The first two products were formed in the largest amounts at temperatures above 250 °C. At 200 or 225 °C, only traces (<3% of the theoretically possible[20] amount) of CF_3CH_2Cl were formed from compounds V–IX. At 250 °C, the amount of CF_3CH_2Cl generated varied from 12% of the theoretical amount (for compound IX) to 60% (for compound VIII). At 300 °C, the amount of this product approached 100% of the theoretical amount possible. Explosion of the sealed glass tubes at 300 °C was attributed to the high internal pressures generated by this gas. Mixtures of $(NPCl_2)_3$ and $[NP(OCH_2CF_3)_2]_3$ also yielded CF_3CH_2Cl when heated at 200 °C (Table I).

The liberation of CF_3CH_2Cl was accompanied by the linkage of rings or chains. Although trimers V and VI yielded open chain polymer at 200 °C, elevation of the temperature to 225 °C resulted in the formation of colorless, insoluble materials believed to be cross-linked linear or cyclomatrix polymers. At 275 or 300 °C, trimers V–VIII were converted to dark-colored pyrolysis products. These were insoluble in organic media but were partly soluble in water.

Cross-linked materials are not accessible if only one chlorine remains on each trimer ring. At temperatures between 200 and 275 °C, compound IX gave CF_3CH_2Cl and colorless, low molecular weight organic-soluble species. These products were examined by combined vapor-phase chromatography and mass-spectrometry techniques. Some of the products were ring-expansion species, as discussed previously, but three of the compounds contained oxygen atoms. These were $N_5P_5Cl(OCH_2CF_3)_7O$ (*m/e* 969), $N_6P_6Cl_3(OCH_2CF_3)_7O$ (*m/e* 1084), and $N_6P_6Cl(OCH_2CF_3)_9O$ (*m/e* 1212).[19] The mass spectral breakdown products were characteristic of those expected from phosphazene *rings* rather than chains (the decompositions resulted mainly from removal of the side groups). The concurrent loss of CF_3CH_2Cl and the appearance of products such as these suggest that P–O–P linkages have been formed. These products have tentatively been assigned structures, such as XIV, XV, or XXI.



XIV



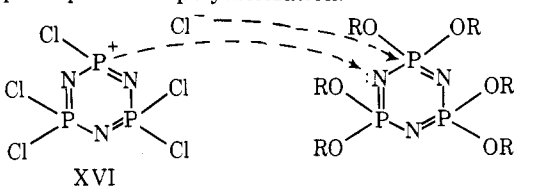
XV

Discussion of the Reaction Mechanisms

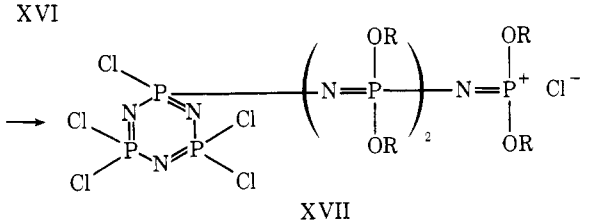
Over-All Reaction Pathways. The interaction of I with X is an exceedingly complex reaction. Three main reaction pathways appear to exist for the formation of mixed substituent polymers, and these are illustrated in Scheme I. The experimental evidence favors the view that all three pathways are accessible in this system.

Pathway 1 provides one of the two plausible mechanisms for the incorporation of "homopolymer" blocks (AAA or CCC sequences) into the mixed substituent polymer. Pathway 2 is compatible with (a) the detection of low concentrations of mixed substituent trimers and tetramers in the reaction mixtures and (b) the demonstrated polymerizability of compounds, such as V, VI, or VII. Moreover, these mixed substituent cyclic species copolymerize with I. Pathway 3 provides explanations for the initial more rapid consumption of I than of X, coupled with the reestablishment of the initial reactant side group ratios in the final polymer. The growth of linear branches of $[NP(OCH_2CF_3)_2]_n$ units on a chain of $(NPCl_2)_n$ units would explain the presence of AAA blocks of $NPCl_2$ and CCC blocks of $NP(OCH_2CF_3)_2$ units.[21] The following sections consider the detailed reaction mechanisms that underlie these pathways.

The Mechanisms of Homopolymerization, Copolymerization, and Ligand Exchange. The mechanism of homopolymerization of $(NPCl_2)_3$ has been studied extensively[12a,22–27] but the process is still only partly understood. The two most plausible mechanisms require initiation either by a thermal ionization of chloride ion from phosphorus (XVI) or by the replacement of a few P–Cl bonds in the system by P–O–H groups following contact with atmospheric moisture.[22] Thus, the presence of P–halogen bonds is presumed to be a prerequisite for polymerization.



XVI

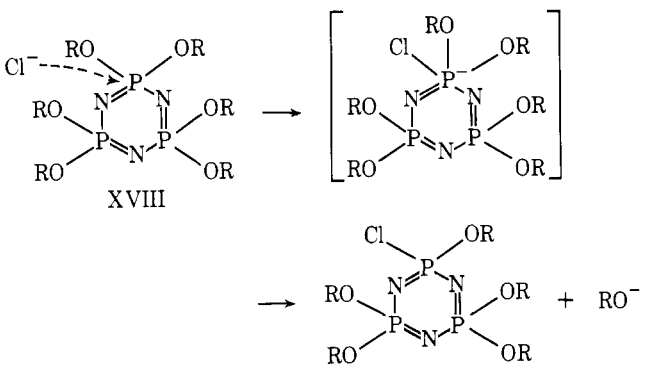


XVII

The present results support this view. No high polymers have yet been prepared from cyclophosphazenes, such as X, that contain only P–organic side-group units. Thus, the simplest mechanism for the direct copolymerization of I with X (pathway 1) requires an attack by species, such as XVI, on the ring nitrogen atoms of X. Concurrent ring cleavage of the attacked molecule would generate a cationic chain propagation process. Presumably, end groups from X residues can add molecules of I, since X does not appear to be an efficient chain terminator.

This role played by P–Cl bonds in initiation is consistent with the observation that the homopolymerization of $N_3P_3(Cl)_x(OCH_2CF_3)_y$ takes place when x is 1–3 but not when more than three trifluoroethoxy groups are present. The presence of two trifluoroethoxy groups per phosphorus may retard chain propagation by sterically restricting an attack by this unit on another similarly hindered molecule. If this explanation is correct, it implies that species such as XVII should add molecules of I but not molecules of X. Hence, blocks of more than three $NP(OCH_2CF_3)_2$ units would not be expected in copolymers formed from I and X. Even if compounds such as VIII, IX, or X could be initiated to yield linear species, the side-group steric effects may favor recyclization rather than linear chain growth.

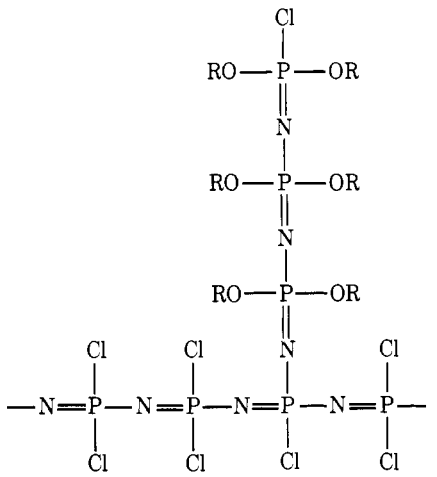
Superimposed on this general polymerization mechanism is the ligand exchange process. The formation of mixed substituent trimers and tetramers in the reaction mixture is unambiguous evidence for this process. Ligand exchange could occur at the cyclic oligomer or the high polymer levels. Such exchange can readily be visualized as a nucleophilic attack by Cl^- on a CF_3CH_2O–P bond, with subsequent or concurrent displacement of $CF_3CH_2O^-$ units (XVIII).[28,29] If this mechanism is correct, ligand exchange and polymerization are competing reactions.



XVIII

Finally, the proposed mechanisms provide a plausible route for the introduction of $NP(OCH_2CF_3)_2$ units as branches attached to a poly(dichlorophosphazene) chain. Thermal ionization of P–Cl middle units in $(NPCl_2)_n$ should occur as readily as in the cyclic trimer. Hence, branches of the type shown in XIX could be formed, and this may offer a facile route for the incorporation of $[NP(OCH_2CF_3)_2]_3$ residues into the copolymer.

The Mechanism of Ring Expansion. The ring-expansion reactions observed with VIII, IX, and X constitute one of the most unusual features of this complex system. Ring expansion to cyclic tetramers and pentamers apparently occurs irrespective of whether P–Cl bonds are present or not (Table III). This may indicate that CF_3CH_2O–P bonds can ionize in the same way as suggested for P–Cl bonds. On the other hand, the preponderance of cyclic tetramers and pentamers formed as products suggests (a) that extensive polymerization and cyclization–depolymerization (equilibration) processes are occurring or (b) that ring cleavage and fragmentation into monomer, linear dimer, and linear trimer units precedes ring expansion or polymerization. No phosphazene monomers,

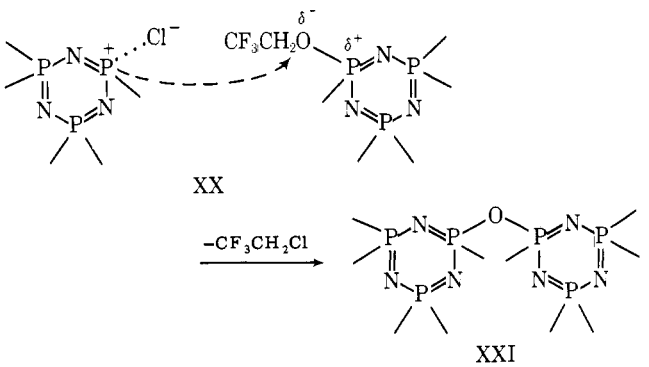


XIX

$N{\equiv}PR_2$, have been detected, but their existence as transient intermediates at high temperatures cannot be excluded. If such species do participate, the copolymerizations can be readily understood and a preference for polymerization or cyclization would be determined by side-group steric factors.[30]

All of these possible mechanisms originate from scrambling reactions among the bonds attached to phosphorus and nitrogen. Presumably, the pathways that participate most to each specific reaction are those that involve cleavage of the most labile bonds. Unfortunately, the relative heterolytic cleavage energies for P–Cl, P–O, and P–N bonds are at present unknown.

The Mechanism of CF_3CH_2Cl Elimination. The formation of CF_3CH_2Cl was observed at temperatures at or above 200 °C whenever both P–Cl and P–OCH_2CF_3 units were present in the same reaction system. As discussed above, polymerization probably involves an attack by cation XVI on the nitrogen atom of another ring. However, the same cation could also attack the oxygen atom of a P–OCH_2CF_3 group, as shown in XX. This latter process would result in the liberation of CF_3CH_2Cl and (a) the generation of a linkage between two or more rings (XXI), (b) the formation of a transannular



XX

XXI

P–O–P linkage (XIV and XV), or (c) the formation of cross-links between chains. It is a reaction that competes directly with polymerization, ring expansion, and ligand exchange, and it appears to have only a slightly higher activation energy than these other processes.

In practice, CF_3CH_2Cl elimination places an upper limit on the temperature that can be employed for the open-chain polymerization of systems that contain both chloro and trifluoroethoxy groups. This limit is between 200 and 225 °C. If polymerization or copolymerization requires a higher temperature (when, for example, more than one trifluoroethoxy group is present on one phosphorus in a homopolymerization process), then CF_3CH_2Cl elimination becomes serious, and cross-linked species are formed.

Experimental Section

Analytical Techniques. Gel permeation chromatograms were obtained with the use of a Waters Associates ALC/GPC 501 instrument fitted with a differential refractive index detector. The columns used were two 1-cm by 60-cm stainless steel columns packed with 10^6 Styragel or four columns packed respectively with 75, 175, 700, and 2000 Å porous glass beads. Tetrahydrofuran or acetone was used as the elution solvent. In both cases, a flow rate of 2.0 mL/min was employed, with sample concentrations of 0.05 to 0.5 wt/vol %. The columns were calibrated with narrow molecular weight distribution polystyrene. However, because the calibration used a different polymer system, the $\bar{M}_n$ values obtained were considered to be only approximate. Their main value was to confirm the presence of medium or high polymers.

Solution viscosity data were obtained with Cannon-Ubbelohde dilution viscometers at concentrations of 1.0, 0.5, 0.33, and 0.25 g/100 mL at 30 °C.

Phosphorus (^{31}P) NMR spectra were obtained on a Jeol PS-100 FT NMR spectrometer in the FT mode, typically with proton decoupling, and 128 scans for the spectra of small molecule compounds and 512 scans for the high polymers. The solvents used were dry benzene or tetrahydrofuran, with the D_2O lock contained in a sealed capillary tube within the 10-mm NMR tubes. Aqueous H_3PO_4 was used as an external standard. The small molecule spectra were obtained for 20 wt % solutions and the polymer spectra were measured for swollen gels.

Vapor-phase chromatography was carried out with the use of a Hewlett-Packard Model 5750 instrument with a 10% UCW-98 column or an OV-17 silicone liquid-phase column on Gas-Chrom Q (Applied Science Labs.). A thermal conductivity detector was employed. The temperature scan was 100 to 200 °C at a rate of 10 °C/min or 25 to 250 °C at a rate of 15 °C/min. The peak areas were calibrated for quantitative work. Mass spectrometric data were obtained with an AEI MS 902 machine and vapor-phase chromatography–mass spectral data were obtained on a Finnigan 3200 instrument with the use of a 170-cm SP 2100 (3% SE-30) VPC column. Infrared spectra were obtained with the use of a Perkin-Elmer 621 grating infrared spectrometer. The detection and quantitative analysis of CF_3CH_2Cl was carried out by means of pressure–volume measurements in a vacuum line system coupled with mass spectrometric and infrared analyses.

Synthesis of Cyclic Phosphazenes. Compounds V–X were synthesized by the methods reported previously.[14] Trimers V–IX were purified to 95% or higher purity by column fractionation and preparative scale gas chromatography. The impurities were small amounts of V–X. For example, the bis(trifluoroethoxy) compound (VII) contained about 3% of the tris(trifluoroethoxy) compound (VII) and 0.5% of the mono(trifluoroethoxy) derivative (V). The hexakis(trifluoroethoxy) trimer (X) and hexachlorocyclotriphosphazene (I) were 100% pure.

Sodium 2,2,2-Trifluoroethoxide (for Polymer Substitutions). Clean sodium (8 g, 0.35 mol) was placed in a nitrogen-purged, 1-L flask fitted with an addition funnel and a reflux condenser. Dry tetrahydrofuran (250 mL) (dried over $LiAlH_4$) was added. Trifluoroethanol (Halocarbon Products) (100 mL, 138 g, 1.38 mol) was then added dropwise with occasional agitation. After the sodium had reacted, additional tetrahydrofuran was added to increase the volume to 500 mL (to give a 0.7 M solution).

Copolymerization of $(NPCl_2)_3$ (I) with $[NP(OCH_2CF_3)_2]_3$ (X) (General Conditions). The two trimers were freshly purified before use. Compound I (El Monte Chem. Corp.) was purified by vacuum sublimation at 50 °C/0.5 Torr, recrystallized once from *n*-heptane, and resublimed three times. Compound X was synthesized by the reaction of CF_3CH_2ONa with I. It was recrystallized once from hot heptane and vacuum sublimed twice at 53 °C to give material, mp 49.5 °C. The two trimers were weighed out in a dry nitrogen-filled dry bag, and the two components were thoroughly mixed before being placed in a constricted heavy-wall polymerization tube. Each tube was evacuated on a vacuum line for 1 h before being sealed. The final dimensions of each sealed tube were 9–10 cm × 1 cm i.d. The tubes were then placed inside a wire gauze shield and heated in a thermoregulated Freas oven at 200 °C. The tube contents were agitated by means of a rocking assembly. After polymerization, the contents of each tube were removed within a nitrogen-filled dry bag. Modifications to this general technique are specified in the following sections.

Copolymerization of I with X. Variation of Reactant Ratios. The data listed in Table I were obtained with the use of the following techniques. Weighed amounts of I and X were sealed in evacuated, thick-walled Pyrex tubes and polymerization was allowed to take place at 200 °C. The polymerization was monitored by inspection of the viscosity of the tube contents and an attempt was made to remove each tube at a point just before gelation occurred. Three sets of duplicate reactions, corresponding to the reactant ratios in Table I, were carried out in order to obtain CF_3CH_2Cl gas yields, ^{31}P NMR spectra, VPC analysis of oligomers, and derivatized materials. The CF_3CH_2Cl yields were determined by vacuum line techniques, as described previously. The ^{31}P NMR spectra were obtained for the products either dissolved in ether (with acetone-d_6 as a lock reagent and trimethyl phosphate or H_3PO_4 as a standard) or used as a swollen gel in tetrahydrofuran or benzene after progressive removal of oligomers by extraction with ether, benzene, and tetrahydrofuran.

Variation of Reaction Time. Individual polymerization tubes, prepared as described previously, were charged with I (1.22 g, 3.5×10^{-3} mol) and X (2.55 g, 3.5×10^{-3} mol) and then evacuated, sealed, and heated at 200 ± 2 °C for 0, 1, 2, 4, 8, 9, 12, 16, 24, 27, 30, 32, 36, 37, 49, and 50 h. Three series of reactions were carried out to duplicate this range of reaction times. Each tube was cooled to 25 °C and opened in a dry bag. The tube contents were then dissolved in dry benzene (10 or 20 mL for different series), and the solutions were analyzed by VPC, ^{31}P NMR, and mass spectrometric techniques. The swollen gelled polymers were extracted three times with benzene or tetrahydrofuran to remove cyclic oligomers and both the extracts and the insoluble polymer were examined by ^{31}P NMR spectroscopy. The results are summarized in Table II.

Derivatization and Analysis of the Products. Compounds I (50.8 g, 0.146 mol) and X (106.8 g, 0.147 mol) were mixed in a Pyrex glass tube, and the tube was evacuated and sealed. The tube was placed in a protective wire gauze bag and was heated in a thermoregulated oven at 200 °C for 33.3 h. The reaction time was chosen to arrest the polymerization at a point just before gelation. The resultant elastomer was soluble in tetrahydrofuran (THF) or methyl ethyl ketone. It was purified by precipitation from THF into pentane. Infrared peaks were observed at the following frequencies (cm^{-1}): 800, 880 (P–O–C); 960 (P–O–C), 1085 (CF_3), 1175 (CF_3), 1280, 1250 (P–N), 1215 (P–O–C), 2950 (CH_2). Microanal. Calcd for 60% I–40% X copolymer: C, 11.53; H, 0.96; F, 27.34; Cl, 25.52; N, 8.40; P, 18.58. Calcd. for 46% I–54% X copolymer: C, 14.06; H, 1.17; F, 33.35; Cl, 17.68; N, 7.59; P, 16.79. Found: C, 14.1; H, 1.47; F, 24.7, 27.25; Cl, 24.0; N, 9.01; P, 16.7. Thus, the polymer contained between 40 and 55% trifluoroethoxy substituent groups.[21]

The copolymer (42.3 g, ~0.36 mol of $NPCl_2$ residues) in dry THF (2 L) was treated dropwise with piperidine (165 mL, 142 g, 1.67 mol). The mixture was then stirred and boiled at reflux for 48 h and stirring was continued at 25 °C for a further 48 h. Filtration of the reaction mixture yielded 75.7 g (0.625 mol) of piperidine hydrochloride. The polymer was isolated by addition of the concentrated filtrate to 95% ethanol followed by reprecipitation from THF into methanol. A Beilstein test demonstrated the presence of residual chlorine. On the assumption that this represented hydrogen chloride bound to the polymer, the polymer solution in THF was treated twice with triethylamine followed by filtration and reprecipitation from THF into methanol and a final wash with water. The resultant product contained no chlorine. It formed clear, flexible films when cast from THF solutions. Anal. Calcd for 60% $NP(NC_5H_{10})_2$–40% $(NP(OCH_2CF_3)_2$ copolymer: C, 40.56; H, 6.04; F, 20.25; N, 13.69; P, 13.76. Calcd. for 55% $NP(NC_5H_{10})_2$–45% $NP(OCH_2CF_3)_2$ copolymer: C, 38.71; H, 5.65; F, 22.64; N, 12.98; P, 13.67. Found: C, 38.50; H, 6.20; F, 19.60; N, 12.80; P, 12.40. Thus, the polymer contained 40–45% of OCH_2CF_3 substituent groups. This value is considered to be more reliable than the value obtained from the chlorotrifluoroethoxy precursor. The infrared spectrum showed peaks at (cm^{-1}): 655 (CF_3); 715 (piperidino); 805, 850 (piperidino); 880 (P–O–C); 900, 955 (piperidino); 1030 (piperidino); 1075 (CF_3); 1110, 1160 (piperidino); 1200, 1250 (P–N); 1330 (piperidino); 1450; 2580, 2950 $(CH_2)_3$. The intrinsic viscosity in THF was 0.71 dL/g and the $\bar{M}_n$ value (by osmometry) was 110 000.

Polymerization and Equilibration of V–X (General Procedure). The trimers were freshly distilled before being sealed in evacuated, heavy-wall Pyrex glass tubes. After being heated, each tube was scored, and one end was cooled in liquid nitrogen to condense any volatile products. The tubes were then opened and connected quickly to a vacuum line for analysis of the volatile products. Oligomeric products were analyzed directly by VPC–mass spectral and infrared techniques. Polymeric products were dissolved in tetrahydrofuran or benzene and, when necessary, derivatized. The best yields of derivatized polymers obtained from several runs were 33% (from V), 68% (from VI), and 85% (from VII). The following procedure is typical.

Polymerization of $N_3P_3Cl_4(OCH_2CF_3)_2$ (VI). A sample of VI (2 mL, 3.4 g, 7.16×10^{-3} mol) was sealed in an evacuated glass tube and heated at 200 °C for 48 h. Volatile products were removed with the

use of a vacuum line, and the nonvolatile components (XII) were subjected to nucleophilic substitution by treatment with a 0.7 M solution (100 mL) (~25% excess) of sodium trifluoroethoxide in tetrahydrofuran. Water was added to remove sodium chloride and precipitate the polymer. The polymer (XIII) was subjected to sublimation conditions at 70 °C/0.1 Torr for 20 h to remove $[NP(OCH_2CF_3)_2]_3$ formed from unpolymerized trimer.[32] The residue (2.24 g, 43%) was then analyzed. Anal. Calcd for $C_4H_4O_2F_6NP$: C, 19.77; H, 1.66; N, 5.76; P, 12.74. Found: C, 20.00; H, 1.47; N, 5.47; P, 13.00. The reduced specific viscosity of a 1% solution in acetone (containing 0.5% Bu_4NBr) was 0.22, and the estimated $\overline{M}_n$ by gel permeation chromatography was 100 000–400 000. By contrast, samples of $[NP(OCH_2CF_3)_2]_n$ prepared from II had reduced specific viscosities of 2.0 or higher, and $\overline{M}_n$ values ranging from 500 000 to 3×10^6.

Acknowledgment. We thank the Firestone Tire and Rubber Co. for the support of this work. We also thank C. W. Cameron for some preliminary experiments and R. D. Minard for the VPC–mass spectrometry data.

References and Notes

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(15) The ^{31}P NMR sign convention used in this paper is the one recently recommended by I.U.P.A.C., i.e., that upfield shifts from H_3PO_4 are reported as negative values and downfield shifts as positive values. This convention is the opposite of the one used in all previous publications from our laboratory and from most other laboratories in North America. The ^{31}P shift ranges given represent values measured in different solvents and in different experiments using the same solvent.
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(17) Concurrent ligand-exchange reactions may also occur, but these were not studied.
(18) The compounds $N_3P_3(OCH_2CF_3)_6$ and $N_3P_3Cl_2(OCH_2CF_3)_4$ were also detected, but these compounds were present as trace impurities in the starting material. The starting material $N_3P_3Cl(OCH_2CF_3)_5$ was also detected.
(19) This parent peak was determined indirectly from the lower molecular weight fragments and the metastable peaks.
(20) Based on the total chlorine and trifluoroethoxy substituent groups present in the initial trimer.
(21) As pointed out by one of the reviewers, the roughly 2:1:1:2 peak ratio of the main peaks in the ^{31}P NMR spectrum of the copolymer would be compatible with a *random* sequencing of AAA and CCC trimer residues, except for the curiously large shift of the presumed AAC peak (at −10.8 ppm) away from the AAA peak at −18.7 ppm. Two explanations for this anomaly seem plausible: (1) The chemical shift for the AAC sequence may be so close to −18.7 that it lies within the base of the AAA peak. The spectra of some polymer samples do, in fact, show a weak peak near −17 ppm. If this explanation is correct, the peak at −10.8 ppm probably represents ligand exchanged units. (2) The polymer may be composed of an AAA-type main chain, with CCC-type branches. If so, sequences of type AAA, CCC, and perhaps CCA′ (at the branch point) would be detectable, but AAC units would not. The branch points would consist of -N=P(N)-(Cl)- (A′) residues, and the chemical shift of such phosphorus atoms may well lie closer to +8.2 ppm than to +18.7 ppm.
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(31) Good microanalysis data for polyphosphazenes are difficult to obtain because of the resistance of these compounds to complete combustion.
(32) Alternatively, the polymer was dissolved in tetrahydrofuran, treated with a tenfold excess of benzene, and centrifuged.

Silicon Phthalocyanine–Siloxane Polymers: Synthesis and ^1H Nuclear Magnetic Resonance Study

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ABSTRACT: The reaction of silicon phthalocyanine (PcSi) disilanols with bis(ureido)dimethylsilane and bis(ureido)siloxanes yields blue PcSi–siloxane polymers of the general formula $[PcSiOSiMePh(OSiMe_2)_nOSiMePhO]$, where Me = methyl, Ph = phenyl, and n = 2 (IV), 3 (V) and 4 (VI). Reactions which lead to polymers V and VI have been studied via ^1H nuclear magnetic resonance spectroscopy. The dominant shielding effect of the Pc ring which causes clear separation of methyl groups in adjacent siloxane chains facilitated this study. Polymers IV and V have been prepared from $PcSi(OSiMePhOH)_2$ and appropriate bis(ureido)siloxanes. Polymer V was considerably more soluble in organic solvents than polymer IV. Polymer V melted at ca. 65–70 °C, while polymer IV softened at ca. 100 °C (T_g?) but did not melt. Molecular weights for IV (1.4×10^4) and V (1.2×10^4) have been estimated from their NMR spectra.

Since the initial synthesis[2] and subsequent development of silicone polymer chemistry there have been a number of reports concerning modified siloxane polymers. Although polymers based on poly(dimethylsiloxane) offer uncommonly good thermal stability, the polymer backbone tends to form a helical structure which facilitates the formation of cyclosiloxanes at elevated temperatures.[3–5] This led to the synthesis of siloxane copolymers containing modified backbones via addition of organic and inorganic groups. Such groups inhibit reversion to cyclics through steric and/or electronic effects and bring about improved thermal stability. To this end, a variety of arylene–siloxane copolymers, e.g., $(-OSi(CH_3)_2-$

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