phosphonium salt, the phosphazene, and the phosphine phosphorus atoms, respectively. The integrated areas of the resonances were in the ratio of 1:1:1.

Reaction of $[NP(OC_6H_5)_2]_3$ with Phenyllithium. A sample of $[NP(OC_6H_5)_2]_3$ (0.5 g, 7.0×10^{-4} mol) was dissolved in THF (100 mL). Phenyllithium (1.2 mL, 7.2×10^{-4} mol) was then added to this solution at 25 °C. The reaction mixture was stirred for 3 h and 2-propanol (2 mL, 0.023 mol) was added to deactivate the organolithium reagent. The reaction solvent was removed by a rotary evaporator, and water (25 mL) was added. The water-insoluble material was then extracted with diethyl ether (25 mL) and the diethyl ether was removed by a rotary evaporator. The diethyl ether soluble product was subjected to mass spectrometric examination. Two parent ions were detected. These were derived from $[NP(OC_6H_5)_2]_3$ (*m/e* 693) and $[NP(OC_6H_5)_5(C_6H_5)]_3$ (*m/e* 677). ^{31}P NMR spectroscopic data of this reaction mixture indicated only one resonance at +8.2 ppm (this is indicative of the presence of $[NP(OC_6H_5)_2]_3$. Thus, $[N_3P_3(C_6H_5)(OC_6H_5)_5]$ was present in small quantities only in the reaction product mixture (probably less that 5%, because the presence of more than 5% would allow for its detection by ^{31}P NMR spectroscopic methods). The presence of any amount of $[N_3P_3(C_6H_5)(OC_6H_5)_5]$ implies that the displacement of lithium phenoxide from $[NP(OC_6H_5)_2]_3$ by phenyllithium is possible and that this displacement reaction is a prospective mechanism for the cross-linking of polymers that possess *p*-lithiophenoxy and *p*-phenoxy substituent groups.

Comparison of the Metal–Halogen Exchange Reaction for Poly(*p*-bromostyrene). A sample of poly(*p*-bromostyrene) (0.5 g, 0.0060 mol) was dissolved in tetrahydrofuran (300 mL). This solution was cooled to −50 °C and *n*-butyllithium (9 mL, 0.0144 mol) was added rapidly. The reaction mixture was stirred for 6 h at −50 °C, and water (9 g, 0.5 mol) was added to deactivate the lithiated species. The reaction mixture was allowed to warm to 25 °C, the reaction mixture was concentrated by rotoevaporation, and the concentrate was added to water. The precipitated polymer was collected by filtration, dried and redissolved in tetrahydrofuran, filtered, and reprecipitated into ethanol. A reprecipitation from tetrahydrofuran into pentane was also carried out. Elemental microanalytical data implied that 15.7% *p*-bromostyrene units remained. Anal. Calcd for $[-(C_8H_8)_x-(C_8H_7Br)_y-]_{n=100}$ ($x = 15.7$ and $y = 84.3$): C, 82.50; H, 6.74; Br, 10.76. Found: C, 81.08; H, 7.22; Br, 10.77. By comparison, the metal–halogen exchange for $[NP(OC_6H_4Br\text{-}p)_2]_n$ (III) resulted in the replacement of approximately 70% of the *p*-bromophenoxy units after the same reaction time. The greater efficiency of the exchange process for poly(*p*-bromostyrene) probably reflects the fact that only one bromine atom is present per repeat unit for this polymer.

Acknowledgment. This work was supported by a grant from the Office of Naval Research.

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(18) Previously reported syntheses of poly(diphenoxyphosphazene)[1] have employed metallic sodium to generate the phenoxide salt; here we report the use of sodium hydride for this purpose.

Synthesis of Alkylphosphazene High Polymers via the Polymerization of Monoalkylpentachlorocyclotriphosphazenes[1,2]

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ABSTRACT: A new class of high molecular weight poly(organophosphazenes) of general formula $[-(N{=}PCl_2)_2{-}N{=}PClR-]_n$ (VIII), where R = CH_3, C_2H_5, *n*-C_3H_7, or *n*-C_4H_9, have been prepared by the thermal polymerization of monoalkylpentachlorocyclotriphosphazenes, $N_3P_3Cl_5R$ (VII). These are among the first high molecular weight polyphosphazenes with side groups linked directly to the skeleton through C–P bonds. Hydrolytically stable, elastomeric derivatives of formula $[-N{=}P(OR')_2)_2{-}N{=}P(OR')R-]_n$, were obtained by a replacement of the chlorine atoms in VIII with trifluoroethoxy or phenoxy groups. Bulky alkyl groups, such as *i*-C_3H_7 or *t*-C_4H_9, retard the polymerization process and sensitize the system to decomposition reactions during polymerization. The structures of the polymers were deduced by comparisons with cyclic trimeric phosphazene model compounds of formulas $N_3P_3(OCH_2CF_3)_5R$ and $N_3P_3(OC_6H_5)_5R$, where R is CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_3H_7, or *t*-C_4H_9.

A broad range of high molecular weight poly(organophosphazenes) can be prepared by the thermal polymerization of hexachlorocyclotriphosphazene (I) to poly(dichlorophosphazene) (II), followed by nucleophilic replacement of the chlorine atoms in II by alkoxy, aryloxy, or amino substituents (Scheme I).[3-7] The resultant organophosphazene derivatives (III, IV, or V) are of fundamental and technological interest.[8-10]

Nevertheless, mechanistic and theoretical arguments can be used to show that polyphosphazenes with organic side

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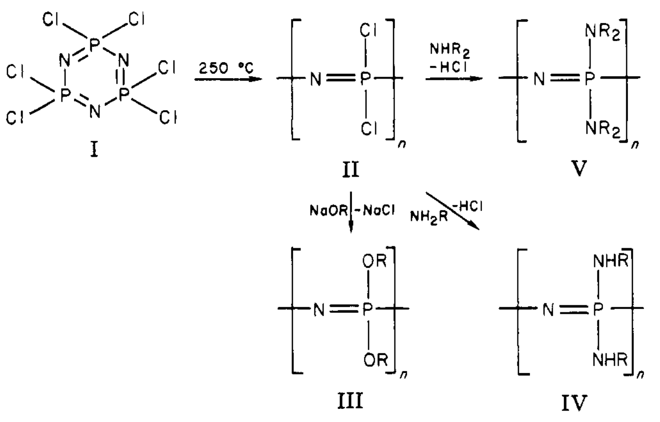
Scheme I



$n \simeq 15\,000$

groups linked directly to phosphorus through C–P bonds should be especially interesting. Specifically, P-C-bonded side groups are expected to be less susceptible to high-temperature thermal rearrangements than P-O- or P-N-bonded side groups, and the presence of, say, methyl groups bonded directly to the phosphazene skeleton should change the intramolecular interactions and generate unexpected physical properties.

Two synthetic routes have been explored for the synthesis of poly(alkyl- or arylphosphazenes). In the first, poly(dihalophosphazenes), such as II, have been allowed to react with organometallic reagents.[11-13] These reactions often lead to cleavage of the polymer skeleton.[12] Only when poly(di*fluoro*phosphazene) is used as a reaction substrate can high degrees of arylation be achieved without extensive chain cleavage.[13] In the second approach, cyclic oligomeric alkyl- or arylphosphazenes have been studied as potential polymerization "monomers".[14,15] Cyclic phosphazenes such as $(NPPh_2)_{3 \text{ or } 4}$ or $(NPMe_2)_{3 \text{ or } 4}$ have so far resisted thermal polymerization.[14,15] Even species such as $(NPClPh)_3$ enter into polymerization processes only in *co*polymerization reactions with $(NPCl_2)_3$ (I).[14]

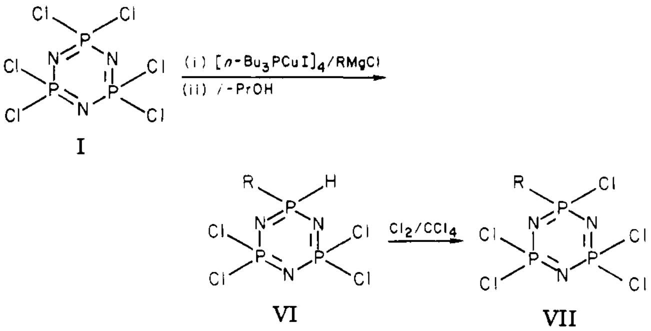
In the present work we have investigated the prospect that monoalkylpentachlorocyclotriphosphazene compounds, $N_3P_3Cl_5R$ (VII), with only *one* alkyl group attached to the cyclic trimeric phosphazene ring, might undergo a ring-opening polymerization to yield high molecular weight polymers with alkyl groups bonded directly to the skeletal phosphorus atoms. This would constitute the simplest and most direct route for the synthesis of alkyl-substituted polyphosphazenes. Moreover, it would allow certain theories to be tested even though the fully alkylated polymers of formula $(NPR_2)_n$ were not available.

The main objectives of the work were to answer the following questions: (1) Is the homopolymerization of chlorocyclophosphazenes inhibited when only one chlorine substituent is replaced by an alkyl group? (2) What effects on the polymerization, if any, would result when a small alkyl group, such as methyl, in VII is replaced by progressively bulkier alkyl groups? (3) In a chlorocyclophosphazene polymerization process, do the monomer residues enter the polymer in the same linkage sequence as the one that exists in the cyclic trimer? Can the presence of one alkyl group attached to the ring be utilized as a probe to monitor this aspect of the polymerization process? (4) What influence might the alkyl groups have on the physical properties of the high polymers?

Results and Discussion

Synthesis of Monoalkylpentachlorocyclotriphosphazenes (VII) (Scheme II). The cyclic trimers

Scheme II

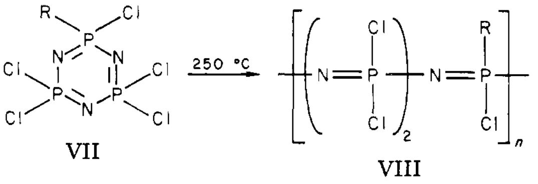


R = CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, or t-C_4H_9

of general structure VII were synthesized by a new technique reported earlier.[16-18] The method involves the interaction of hexachlorocyclotriphosphazene (I) with alkyl Grignard reagents in the presence of $[n\text{-}Bu_3PCuI]_4$,[19] followed by treatment of the reaction intermediate[16] with 2-propanol, to yield *hydrido*phosphazenes (VI).[16,17] Subsequent treatment of VI with chlorine in tetrachloromethane solution led to the formation, in high yield, of the monoalkylpentachlorocyclotriphosphazenes (VII).[17,18] For this study, compounds were prepared in which the R group was CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, or t-C_4H_9. The characterization data for these compounds have been discussed in another paper.[18]

Rigorous steps were taken to ensure the purity of the monoalkylpentachlorocyclotriphosphazene compounds (VII) before polymerization was attempted. The purification procedure involved successive recrystallizations from n-hexane, followed by vacuum sublimation or distillation. This procedure was repeated until only one sharp peak was observed when the compound was subjected to vapor phase chromatography/mass spectrometric analysis.[20]

Polymerization of VII. Four of the rigorously purified monoalkylpentachlorocyclotriphosphazenes (VII) underwent a thermal polymerization at 250 °C to yield high polymers of general formula VIII. However, marked differences in the polymerization behavior were observed, depending on the size of the alkyl group in VII. Those cyclic trimers which contained small alkyl groups, such as methyl or ethyl, were found to polymerize readily within 15–24 h at 250 °C. When R was n-C_3H_7 or n-C_4H_9, longer polymerization times were required (18–36 h), but polymers of type VIII were still formed. However, those species in which R was i-C_3H_7 or t-C_4H_9 polymerized at a slower rate and yielded discolored cross-linked products. Hydrogen chloride was also liberated during these latter reactions. The mechanisms of these reactions will be discussed in a later section.



Replacement of Chlorine in VIII. Model Compound Studies. Phosphazene polymers that contain P–Cl bonds are hydrolytically unstable.[3-7] Thus, full characterization of polymers VIII could be undertaken only after the halogen atoms had been replaced by organic residues. However, the reactions of phosphazene high polymers are nearly always more complex than those of the analogous small-molecule phosphazenes. Here, in this work (as well as in many of our previous studies[21]), it was necessary to

Table I
Model Compounds: Characterization Data

		mass spectral data[32]			elemental anal.[33,34]	
compd		found	calcd		found	calcd
$N_3P_3(OCH_2CF_3)_5(CH_3)$	oil	645	645	C	20.11	20.49
				H	2.27	2.20
				N	6.46	6.51
				P	14.30	14.40
$N_3P_3(OCH_2CF_3)_5(C_2H_5)$	31	659	659		658.9969	658.9984
$N_3P_3(OCH_2CF_3)_5(n\text{-}C_3H_7)$	49	673	673		673.0156	673.0141
$N_3P_3(OCH_2CF_3)_5(n\text{-}C_4H_9)$	32	687	687		687.0286	687.0297
$N_3P_3(OCH_2CF_3)_5(i\text{-}C_3H_7)$	26	673	673		673.0144	673.0141
$N_3P_3(OCH_2CF_3)_5(t\text{-}C_4H_9)$	oil	687	687		687.0281	687.0297
$N_3P_3(OC_6H_5)_5(CH_3)$	56	615	615	C	60.50	60.53
				H	4.60	4.55
				N	6.80	6.82
				P	15.10	15.09
$N_3P_3(OC_6H_5)_5(C_2H_5)$	84	629	629		629.1386	629.1398
$N_3P_3(OC_6H_5)_5(n\text{-}C_3H_7)$	66	643	643		643.1560	643.1554
$N_3P_3(OC_6H_5)_5(n\text{-}C_4H_9)$	oil	657	657		657.1708	657.1711
$N_3P_3(OC_6H_5)_5(i\text{-}C_3H_7)$	oil	643	643		643.1550	643.1554
$N_3P_3(OC_6H_5)_5(t\text{-}C_4H_9)$	oil	657	657		657.1701	657.1711

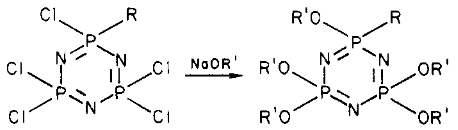
Table II
Model Compounds: NMR Data[a]

	^{31}P NMR data,[35,b] ppm		^1H NMR data,[36] δ			
compd	P(R)(OR′)	$P(OR')_2$	R		R′	coupling constants,[d] Hz
$N_3P_3(OCH_2CF_3)_5(CH_3)$	38.3 (t)	14.3 (d)	CH_3	1.6 (dt)	4.2 (m)	$J_{PNP} = 47.6$ $J_{PCH} = 17.0$ $J_{PNPCH} = 2.1$
$N_3P_3(OCH_2CF_3)_5(C_2H_5)$	43.8 (t)	16.1 (d)	$\mathit{CH_2}CH_3$ $CH_2\mathit{CH_3}$	1.8 (m) 1.0 (dt)	4.1 (m)	$J_{PNP} = 43.1$ $J_{PCCH} = 22.5$ $J_{HCCH} = 7.5$
$N_3P_3(OCH_2CF_3)_5(n\text{-}C_3H_7)$	42.1 (t)	16.0 (d)	$\mathit{CH_2CH_2}CH_3$ $CH_2CH_2\mathit{CH_3}$	1.7 (m) 0.9 (t)	4.2 (m)	$J_{PNP} = 42.9$ $J_{HCCH} = 7.0$
$N_3P_3(OCH_2CF_3)_5(n\text{-}C_4H_9)$	42.5 (t)	16.1 (d)	$(\mathit{CH_2})_3CH_3$ $(CH_2)_3\mathit{CH_3}$	1.8 (m) 0.9 (t)	4.1 (m)	$J_{PNP} = 43.6$ $J_{HCCH} = 7.2$
$N_3P_3(OCH_2CF_3)_5(i\text{-}C_3H_7)$	46.7 (t)	16.5 (d)	$\mathit{CH}(CH_3)_2$ $CH(\mathit{CH_3})_2$	1.9 (m) 1.1 (dd)	4.1 (m)	$J_{PNP} = 40.2$ $J_{PCCH} = 20.8$ $J_{HCCH} = 6.5$
$N_3P_3(OCH_2CF_3)_5(t\text{-}C_4H_9)$	67.3 (t)	16.4 (d)	$C(CH_3)_3$	1.2 (d)	4.1 (m)	$J_{PNP} = 20.1$ $J_{PCCH} = 21.5$
$N_3P_3(OC_6H_5)_5(CH_3)$	35.9 (t)	8.7 (d)	CH_3	1.2 (dt)	7.1 (m)	$J_{PNP} = 49.2$ $J_{PCH} = 17.1$ $J_{PNPCH} = 1.2$
$N_3P_3(OC_6H_5)_5(C_2H_5)$	40.1 (t)	8.9 (d)	$\mathit{CH_2}CH_3$ $CH_2\mathit{CH_3}$	1.5 (m) 0.8 (dt)	7.1 (m)	$J_{PNP} = 43.3$ $J_{PCCH} = 21.5$ $J_{HCCH} = 7.0$
$N_3P_3(OC_6H_5)_5(n\text{-}C_3H_7)$	38.4 (t)	8.7 (d)	$\mathit{CH_2CH_2}CH_3$ $CH_2CH_2\mathit{CH_3}$	1.4 (m) 0.8 (t)	7.0 (m)	$J_{PNP} = 42.3$ $J_{HCCH} = 6.5$
$N_3P_3(OC_6H_5)_5(n\text{-}C_4H_9)$	38.7 (t)	8.8 (d)	$(\mathit{CH_2})_3CH_3$ $(CH_2)_3\mathit{CH_3}$	1.3 (m) 0.6 (t)	7.0 (m)	$J_{PNP} = 43.3$ $J_{HCCH} = 7.0$
$N_3P_3(OC_6H_5)_5(i\text{-}C_3H_7)$	43.3 (t)	9.7 (d)	$\mathit{CH}(CH_3)_2$ $CH(\mathit{CH_3})_2$	1.8 (m) 0.9 (dd)	7.1 (m)	$J_{PNP} = 43.3$ $J_{PCCH} = 20.0$ $J_{HCCH} = 6.5$
$N_3P_3(OC_6H_5)_5(t\text{-}C_4H_9)$	65.5 (t)	8.1 (d)	$C(CH_3)_3$	0.95 (d)	7.0 (m)	$J_{PNP} = 16.7$ $J_{PCCH} = 21.0$

[a] d = doublet, t = triplet, m = unresolved multiplet. [b] THF solution. [c] $CDCl_3$ solution. [d] Couplings unresolved if not listed.

examine the halogen-substitution behavior of cyclic species such as VII as a prelude to performing substitution reactions with the analogous high polymers VIII. In this way, we hoped to optimize the substitution reaction conditions and verify that the alkyl groups would not inhibit complete replacement of the halogen atoms or sensitize the system to skeletal cleavage reactions.

All compounds of type VII were found to react cleanly with sodium trifluoroethoxide[22,23] or sodium phenoxide[24] to form the products of formula IX in high yield. Species IX were characterized by the use of a combination of infrared,[25,26] ^1H, and ^{31}P NMR spectroscopy, mass spectrometry (both low and high resolution) and, in representative cases, elemental analysis. These data are listed in Tables I and II.



VII IX

R′ = CH_2CF_3, C_6H_5; R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$

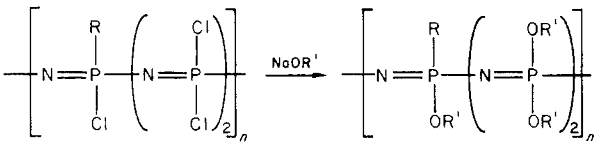
The total replacement of halogen in compounds VII occurred smoothly with all variations of the alkyl group,

Table III
Polymers: Characterization Data

polymer	$\overline{M}_n$(GPC)[37]	T_g,[38] °C		elemental anal.[34] found	calcd
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(CH_3)-]_n$	1.5×10^6	−50	C	20.40	20.42
			H	2.16	2.01
			N	6.50	6.48
			P	14.51	14.36
			F	43.51	44.04
			Cl	0.64	
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(C_2H_5)-]_n$	1.0×10^6	−58	C	21.75	21.87
			H	2.18	2.27
			N	6.35	6.37
			P	14.10	14.09
			F	43.17	43.23
			Cl	0.20	
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(n\text{-}C_3H_7)-]_n$	9.0×10^5	−55	C	23.00	23.20
			H	1.90	1.93
			N	6.24	6.24
			P	13.84	13.80
			F	42.00	42.34
			Cl	0.22	
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(n\text{-}C_4H_9)-]_n$	9.0×10^5	−53	C	24.36	24.48
			H	2.83	2.77
			N	6.16	6.11
			P	13.74	13.52
			F	39.47	41.48
			Cl	0.10	
$[-(N{=}P(OC_6H_5)_2)_2{-}N{=}P(OC_6H_5)(CH_3)-]_n$	1.2×10^6	−15	C	60.32	60.52
			H	4.66	4.55
			N	6.71	6.82
			P	15.12	15.09
			Cl	0.05	

R. The reactions of VII with sodium trifluoroethoxide were found to proceed readily in boiling tetrahydrofuran. However, the reactions with sodium phenoxide required the use of boiling 1,4-dioxane as a solvent to achieve complete substitution.

Replacement of Chlorine in VIII. Macromolecular Systems. After the optimum conditions for halogen replacement with trifluoroethoxy or phenoxy groups had been determined for the cyclic model compounds VII, these conditions were employed for halogen-replacement reactions with polymers of type VIII. All four polymers of type VIII, where R was CH_3, C_2H_5, n-C_3H_7, or n-C_4H_9, reacted with sodium trifluoroethoxide with complete replacement of the chlorine atoms to yield the hydrolytically stable derivatives of formula X ($R' = CH_2CF_3$). Polymer VIII ($R = CH_3$) was also allowed to react with sodium phenoxide to yield X ($R' = C_6H_5$). Particular interest was associated with those polymers of type X that contained trifluoroethoxy units as the cosubstituent groups because a considerable amount of structural and chemical information is available for the related homopolymer of formula $[NP(OCH_2CF_3)_2]_n$.[4,6,9]



VIII X

$R = CH_3, C_2H_5, n\text{-}C_3H_7, n\text{-}C_4H_9;\ R' = CH_2CF_3$
$R = CH_3;\ R' = C_6H_5$

Characterization and Properties of the Polymers. All of the polymers of types VIII and X were characterized by means of infrared, ^1H, and ^{31}P NMR spectroscopy. In addition, glass transition temperatures (T_g), GPC molecular weights, and elemental analyses were obtained for polymers of type X. The results are summarized in Tables III and IV.

The infrared spectra[25-27] of the polymers were compatible with structures VIII and X, with an intense absorption detected between 1100 and 1300 cm^{-1}. This is characteristic of the —P=N— skeleton.[6] The spectra of polymers of type VIII also showed evidence for the presence of the alkyl groups. The ^1H and ^{31}P NMR data for polymers VIII and X are listed in Table IV. The ^1H NMR spectra of VIII were compatible with the presence of the alkyl groups: a broad resonance was detected, centered between δ 1.0 and 1.5. The ^1H NMR spectra of polymers X showed two areas of resonance. The resonance from the alkyl group appeared between δ 1.0 and 1.5. The resonance position for the trifluoroethoxy cosubstituent appeared as a broad multiplet centered at δ 4.2, while the phenoxy substituent showed a resonance position of δ 7.1. An integration of the areas under these two sets of peaks suggested a ratio of one alkyl group per five trifluoroethoxy or phenoxy constituents.

The ^{31}P NMR spectra of polymers VIII and X showed two general areas of resonance with considerable fine structure in each region. Representative spectra are shown in Figure 1. An integration of the areas under the two envelopes indicated a ratio of 1:2 for the two types of phosphorus atoms present. This was again compatible with the conclusion that an average of one alkyl group per three phosphorus atoms was retained in polymers VIII and X. The fine structure found within the two ^{31}P NMR envelopes was consistent with a variety of microenvironments for the phosphorus atoms in the skeleton, perhaps complicated by P–P spin–spin or through-space coupling. In any case, it seems clear that the spectra are too complicated to be explained by a *regular* sequencing of repeating sets of the type depicted in VIII and X. Thus, it would appear that the polymerization mechanism of VII does *not* involve a simple ring cleavage at one specific site

Table IV
Polymers: NMR Data[a]

polymer	^{31}P NMR data,[35] ppm: P(R)(OR′) or P(R)Cl	^{31}P NMR data,[35] ppm: P(OR′)$_2$ or PCl$_2$	^{1}H NMR data,[36] ppm: R	^{1}H NMR data,[36] ppm: R′
$[-(N{=}PCl_2)_2{-}N{=}PCl(CH_3)-]_n$	10.2 (m)	−21.0 (m)	1.5 (m)	
$[-(N{=}PCl_2)_2{-}N{=}PCl(C_2H_5)-]_n$	17.4 (m)	−19.8 (m)	1.3 (m)	
$[-(N{=}PCl_2)_2{-}N{=}PCl(n\text{-}C_3H_7)-]_n$	17.3 (m)	−20.1 (m)	1.2 (m)	
$[-(N{=}PCl_2)_2{-}N{=}PCl(n\text{-}C_4H_9)-]_n$	17.3 (m)	−21.3 (m)	1.1 (m)	
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(CH_3)-]_n$	17.4 (m)	−8.5 (m)	1.5 (m)	4.2 (m)
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(C_2H_5)-]_n$	22.9 (m)	−7.8 (m)	1.4 (m)	4.2 (m)
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(n\text{-}C_3H_7)-]_n$	19.3 (m)	−8.2 (m)	1.2 (m)	4.2 (m)
$[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(n\text{-}C_4H_9)-]_n$	21.0 (m)	−8.3 (m)	1.2 (m)	4.2 (m)
$[-(N{=}P(OC_6H_5)_2)_2{-}N{=}P(OC_6H_5)(CH_3)-]_n$	11.0 (m)	−19.1 (m)	1.2 (m)	7.1 (m)

[a] All resonances appeared as complex unresolved multiplets. No coupling constants could be determined. m = multiplet.

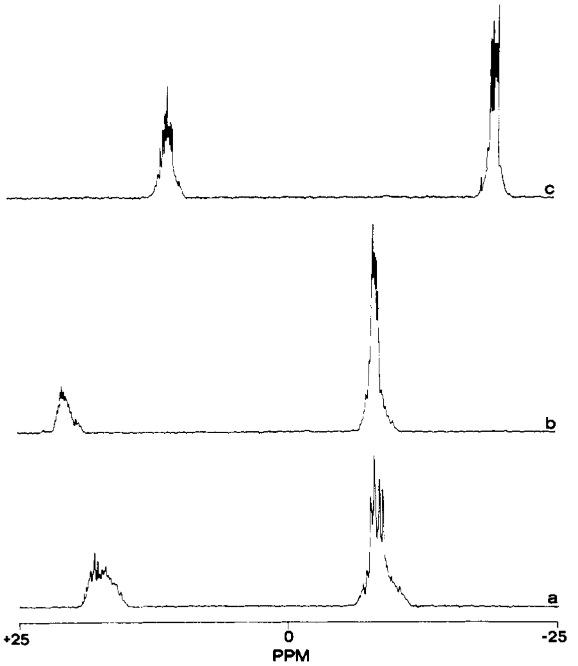


Figure 1. Representative ^{31}P NMR spectra of polymers X: (a) $[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(CH_3)-]_n$; (b) $[-(N{=}P(OCH_2CF_3)_2)_2{-}N{=}P(OCH_2CF_3)(n\text{-}C_4H_9)-]_n$; (c) $[-(N{=}P(OC_6H_5)_2)_2{-}N{=}P(OC_6H_5)(CH_3)-]_n$.

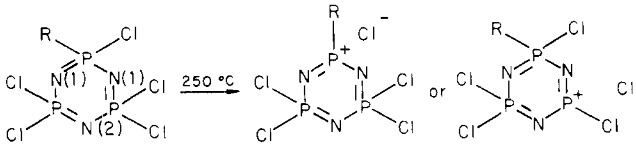
followed by an ordered coupling of the linear trimeric fragments. This aspect is discussed in more detail in a later section.

The low-temperature properties of polymers of type X were not affected significantly by the presence or the type of the alkyl group, R, bound to the polymer. The glass transition temperatures (listed in Table III) of polymers X were found to be 10–15 °C higher than those of the related *homo*polymers $[NP(OCH_2CF_3)_2]_n$ (T_g = −66 °C) or $[NP(OC_6H_5)_2]_n$ (T_g = −8 °C). However, the room-temperature physical properties of polymers X were very different from those of the *non*alkylated analogues. Poly[bis(trifluoroethoxy)phosphazene] is a microcrystalline, film-forming polymer.[3,4] The trifluoroethoxy derivatives of polymers X were elastomers, although the elasticity decreased as the size of the alkyl group increased. The methyl derivative could be stretched readily to 400% of its original length without rupture, while the *n*-butyl polymer was less extensible (~50% extension before rupture). The phenoxy derivative of polymer X (R = CH_3, R′ = C_6H_5) also displayed elastomeric properties and could be reversibly extended by ~200% without breakage.

The appearance of elastomeric properties following the introduction of the alkyl group R in polymers X was attributed to the role played by the alkyl units in disrupting the molecular symmetry, thereby reducing microcrystalline order.

Polymerization Mechanism. The mechanism of polymerization of $(NPCl_2)_3$ (I) is still only poorly understood even though this reaction has been studied in some detail.[6] Nevertheless, convincing evidence exists that phosphorus–halogen bonds are a prerequisite for polymerization. It has been suggested that the ionization of a chloride ion from phosphorus (perhaps catalyzed by trace impurities) is an essential requirement for the initiation process.[28–31] It seems reasonable to assume that the mechanism of polymerization of VI is similar to that of I.

Thus, transient intermediates or transition states of the type depicted in XI or XII may participate in the initiation



VII XI XII

process, with subsequent steps involving a ring-opening attack by the phosphazenium cations XI or XII on the N(1) or N(2) skeletal atoms of VII. If this is true, a high probability exists that a statistically random arrangement of PCl(R) and PCl_2 groups will be found in the final polymer, even though the ratio of these species remains at 1:2. This interpretation is compatible with the complex patterns observed in the ^{31}P NMR spectra of these polymers (see Figure 1). Any alternative interpretation would require a 100% preference for the formation of, say, species XI over XII *and* a 100% preference for attack at, say, N(1) over N(2). This is highly unlikely. Moreover, because the 1:2 ratio of repeating units was retained in the polymer, it appears that the polymerization mechanism does not involve a prior breakdown of the trimer to a *monomer*. Monomer units of type $N{\equiv}PCl(R)$ would be expected to have a different reactivity in addition reactions from those of type $N{\equiv}PCl_2$.

However, the alkyl group does appear to influence the polymerization process. The molecular weights of the polymers X showed a small but definite decrease as the size of the alkyl group, R, was increased (Table III). Also, the time required for polymerization increased with increasing steric bulk of the alkyl group. These results may be ascribed to steric effects involving attack by species such as XI on another trimer ring. Alternatively, they may reflect the influence of side reactions. The detection of hydrogen chloride as a product from the polymerization of $N_3P_3Cl_5(i\text{-}C_3H_7)$ or $N_3P_3Cl_5(t\text{-}C_4H_9)$, together with concurrent cross-linking, is an indication that alkyl groups (and especially branched alkyl groups) cannot survive intact for extended periods of time in the relatively hostile environment needed to effect polymerization.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, obtained from El Monte Chemical Corp., was purified by fractional sublimation followed by recrystallization from *n*-hexane, to a final melting point of 111.5–112.5 °C. The Grignard reagents were commercial products obtained from Aldrich or Alfa Ventron. The copper complex $[n\text{-}Bu_3PCuI]_4$ was prepared as reported in the literature.[19] Tetrahydrofuran (THF) (obtained from Fisher) was distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium–benzophenone ketyl drying agent. The 1,4-dioxane (obtained from Fisher) was distilled in a similar manner from sodium metal. Trifluoroethanol (obtained from Halocarbon Products), was dried over molecular sieves (4 Å) before use. The phenol (obtained from Fisher) was used as received.

Synthesis of $N_3P_3Cl_5R$. All compounds of structure VII (R = CH_3, C_2H_5, $n\text{-}C_3H_7$, $n\text{-}C_4H_9$, $i\text{-}C_3H_7$, $t\text{-}C_4H_9$) were prepared as described earlier.[16–18] These compounds were purified for polymerization by either recrystallization and sublimation or by distillation. The compounds were considered "pure" when the vapor phase chromatography/mass spectrometric trace showed only one sharp peak.

Polymerization Techniques. All attempts to polymerize VII were carried out in an identical manner; the following procedure is typical. Monomethylpentachlorocyclotriphosphazene, $N_3P_3Cl_5CH_3$ (5.0 g, 0.015 mol), purified as described above, was placed in a Pyrex glass tube (13 mm o.d. × 200 mm) that was constricted $\simeq$50 mm from the open end of the tube. The tube was attached to a vacuum line and was evacuated for 30 min, after which time the pressure in the system was 0.05 torr. The tube was then sealed at the constriction, wrapped in aluminum gauze, and placed on a rocking device in a Freas thermoregulated oven, preheated to a temperature of 250 °C. The viscosity of a molten reaction mixture increased during the next 15–36 h. The tube was removed from the oven and allowed to cool to room temperature. The tube was then opened in a nitrogen-filled glovebag and the contents were transferred to a small sublimator. The unpolymerized cyclic trimer was then sublimed from the polymer at 70 °C (0.05 torr). Typical conversions to polymer ranged from 50 to 75%.

When this technique was applied to $N_3P_3Cl_5R$ (R = $i\text{-}C_3H_7$, $t\text{-}C_4H_9$), the contents of the tube discolored before any obvious increase in viscosity was noted. Prolonged heating of these compounds (48 h) resulted in the formation of a brown, insoluble material. Hydrogen chloride was detected when the tubes were opened.

Model Compound Halogen Replacement Studies. (a) Reactions with $NaOCH_2CF_3$. The reactions of all cyclic compounds $N_3P_3Cl_5R$ (VII) with $NaOCH_2CF_3$ were carried out in an identical manner. The following is a typical procedure. A solution of sodium trifluoroethoxide in THF (125 mL) was prepared from sodium (3.5 g, 0.15 mol) and trifluoroethanol (20.0 g, 0.20 mol) under an atmosphere of dry nitrogen. A solution of $N_3P_3Cl_5CH_3$ (5.0 g, 0.015 mol), dissolved in THF (50 mL), was added slowly to the solution of sodium trifluoroethoxide. When the addition was complete, the reaction mixture was heated to reflux for 48 h. After this time, the reaction mixture was allowed to cool to room temperature, poured into water (250 mL), and extracted with diethyl ether (2 × 250 mL). The ether layer was dried over magnesium sulfate, and the ether was removed under reduced pressure, to leave the crude products as an oil. The product was purified by filtration of a solution in CH_2Cl_2 through neutral alumina and finally by recrystallization from *n*-hexane. Characterization data for the products are listed in Tables I and II.

(b) Reactions with $NaOC_6H_5$. A similar technique was employed for the reactions of cyclic compounds $N_3P_3Cl_5R$ (VII) with $NaOC_6H_5$. However, it was found that complete substitution was effected more readily in 1,4-dioxane at reflux temperature. The following procedure is typical. A solution of sodium phenoxide in 1,4-dioxane (125 mL) was prepared from sodium (4.5 g, 0.19 mol) and phenol (20.0 g, 0.21 mol) under an atmosphere of dry nitrogen. A solution of $N_3P_3Cl_5CH_3$ (5.0 g, 0.015 mol), dissolved in 1,4-dioxane (50 mL), was added slowly to the solution of sodium phenoxide. When the addition was complete, the reaction mixture was heated to reflux for 48 h. After this time, the reaction mixture was allowed to cool to room temperature, poured into water (250 mL), and extracted with diethyl ether (2 × 250 mL). The ether layer was dried over magnesium sulfate, and the ether was removed under reduced pressure. This left the product contaminated with some phenol. The excess phenol was removed by vacuum distillation [60 °C (0.05 torr)], to leave the crude product as an oil. The compound was purified further by filtration of a solution in CH_2Cl_2 through neutral alumina. The characterization data for the products are listed in Tables I and II.

Polymer Substitution Reactions. (a) Reactions with $NaOCH_2CF_3$. The experimental conditions found to be effective for halogen replacement in the model compound studies were also employed for substitution reactions with polymers of type VIII. The following is a typical procedure. Polymer VIII, $[-(N{=}PCl_2)_2{-}N{=}PClR-]_n$ (5.0 g), was dissolved in THF (200 mL) and the mixture was added dropwise over 1 h to a solution of sodium trifluoroethoxide [made from sodium (3.5 g, 0.15 mol) and trifluoroethanol (20 g, 0.20 mol) in THF (200 mL)]. When the addition was complete, the solution was heated to reflux for 48 h. After this time, the solution was allowed to cool to room temperature, concentrated to one-third of its original volume, and poured into 2% aqueous HCl solution (1 L). The polymer which precipitated from this solution was filtered off, dissolved in a minimum amount of THF, and reprecipitated into hexane (500 mL). This alternating reprecipitation into water and hexane was continued until a clear, colorless solution of the polymer in THF was obtained. A final reprecipitation into hexane was then performed and the resultant polymer was dried for 24 h in vacuo.

(b) Reaction with $NaOC_6H_5$. Polymer VIII, $[-(N{=}PCl_2)_2{-}NPCl(CH_3)-]_n$ (5.0 g), was dissolved in 1,4-dioxane (200 mL) and the mixture was added dropwise over 1 h to a solution of sodium phenoxide [made from sodium (4.5 g, 0.19 mol) and phenol (20.0 g, 0.21 mol) in 1,4-dioxane (200 mL)]. When the addition was complete, the solution was heated to reflux for 60 h. After this time, the solution was allowed to cool to room temperature, concentrated to half its original volume, and poured into 2% aqueous NaOH solution (1 L). The polymer which precipitated from this solution was purified as described previously for the trifluoroethoxy derivatives. The characterization data for all the polymers are listed in Tables III and IV.

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(36) ^1H NMR spectra were recorded on a JEOL JNM-PS-100 spectrometer operating at 100 MHz in the Fourier transform mode. The samples were dissolved in C_4D_8O (polymers) or $CDCl_3$ (cyclic species). The data were processed on a Nicolet 1080 computer. Peak assignments and coupling constants were determined on the basis of ^{31}P-decoupled and undecoupled spectra. Chemical shifts are on the δ scale and referenced to internal tetramethylsilane.
(37) The molecular weights were estimated by gel permeation chromatography, using polystyrene standards with 10^6, 10^5, 10^4, and 10^3 Styragel columns in series. The solvent was tetrahydrofuran.
(38) The glass transition temperatures (T_g) were measured with the use of a Chemical Instruments Corp. torsional braid analyzer, programmed to operate from −120 to +120 °C, with a temperature scan rate of 2.0 °C min^{-1}.

Phosphazene High Polymers with Steroidal Side Groups[1]

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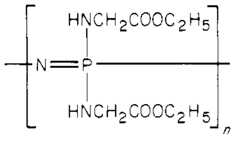
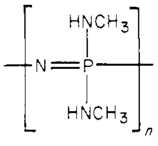
ABSTRACT: Steroidal residues derived from desoxoestrone (III), estrone (IV), 17β-estradiol (V), 17α-ethynylestradiol (VI), estradiol 3-methyl ether (VII), and 1,4-dihydroestradiol 3-methyl ether (VIII) have been linked to a polyphosphazene chain via the sodium salt of the steroidal hydroxy function. The degree of replacement of P–Cl bonds by P–OR units was in the range 0.5–40%, depending on the reaction conditions. The residual chlorine atoms were removed by reaction with methylamine, ethyl glycinate, or *n*-butylamine. Stable polymers of structure XIV were obtained when the steroidal units were linked to phosphorus through an aryloxy residue. However, linkage through an alkoxy residue led to instability and chain cleavage. The use of ethyl glycinato residues as cosubstituent groups yielded hydrolytically degradable polymers. Comparisons are made between these high-polymeric reactions and those of small-molecule cyclophosphazene models.

The use of macromolecules as carrier species for biologically active agents is a subject of growing interest.[2-4] Poly(organophosphazenes) are of particular interest in this respect. Amino acid ester substituted polyphosphazenes (I) are potential biodegradable polymers,[5] and the water-soluble polymer II has been investigated as a polymeric coordination ligand for platinum anticancer complexes.[6]



$$\left[-N{=}P(NHCH_2COOC_2H_5)_2- \right]_n$$

I

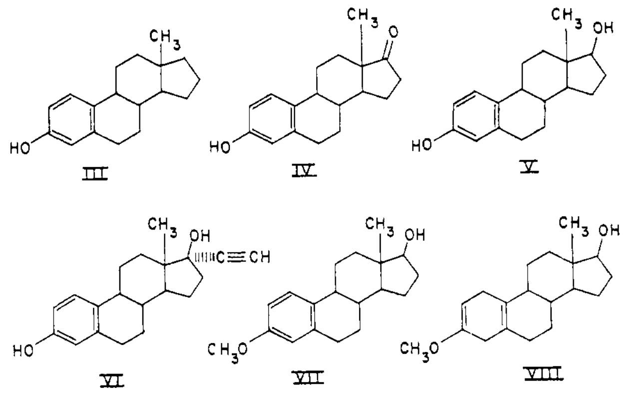


$$\left[-N{=}P(NHCH_3)_2- \right]_n$$

II

In this paper, we consider the prospect that poly(organophosphazenes) can be linked covalently to biologically active species, such as steroids. As a prelude to this study, we reported elsewhere the synthesis of several steroidal phosphazene model compounds based on the small-molecule cyclotriphosphazene framework XI.[7] In that work, we identified six steroid structures that were suitable for attachment to a phosphazene skeleton. These were desoxoestrone (III), estrone (IV), 17β-estradiol (V), 17α-ethynylestradiol (VI), estradiol 3-methyl ether (VII), and 1,4-dihydroestradiol 3-methyl ether (VIII). Here we extend those model reactions to the high polymers.

Chart I



Steroids III, VII, and VIII were used because they contain only one active functional group and should not participate in cross-linking reactions. Steroid VIII was utilized because it can be converted, by treatment with acid, to 19-nortestosterone, a clinically important species.[8] Steroids IV–VI are also pharmacologically active. Although they are multifunctional, species IV–VI possess a 3-C-aromatic hydroxy function that should be more reactive than the hydroxy or keto groups at the 17-positions. Hence, cross-linking was expected to be minimal. The residues from III–VII were expected to confer a characterization advantage because their presence can be monitored by ultraviolet spectroscopy. Species IV–VI were expected to be biologically active, even in the polymer-bound form because the functionally active centers would remain exposed.

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