(9) Webster, O. W.; Hertler, W. R.; Sogah, D. Y.; Farnham, W. B.; RajanBabu, T. V. *J. Am. Chem. Soc.* **1983**, *105*, 5706.
(10) Allcock, H. R. *Acc. Chem. Res.* **1978**, *11*, 81.
(11) Allcock, H. R.; Siegel, L. A. *J. Am. Chem. Soc.* **1964**, *86*, 5140.
(12) Siegel, L. A.; van den Hende, J. H. *J. Chem. Soc. A* **1967**, 817.
(13) Allcock, H. R.; Teeter-Stein, M. *J. Am. Chem. Soc.* **1974**, *96*, 49.
(14) Allcock, H. R.; Teeter-Stein, M.; Bissell, E. C. *J. Am. Chem. Soc.* **1974**, *96*, 4795.
(15) Allcock, H. R.; Allen, R. W.; Bissell, E. C.; Smeltz, L. A.; Teeter, M. *J. Am. Chem. Soc.* **1976**, *98*, 5120.
(16) Allcock, H. R.; Ferrar, W. T.; Levin, M. L. *Macromolecules* **1982**, *15*, 697.
(17) Allcock, H. R. In "Inclusion Compounds"; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Eds. Academic Press: New York, 1984; Vol. 1.
(18) Finter, J.; Wegner, G. *Makromol. Chem.* **1979**, *180*, 1093.
(19) Takemoto, K.; Miyata, M. *Macromol. Sci.-Rev.-Macromol. Chem.* **1980**, *C18*, 83.
(20) Farina, M.; Natta, G.; Allegra, G.; Loffelholz, M. *J. Polym. Sci., Part C* **1967**, *16*, 2517.
(21) Allcock, H. R.; Walsh, E. J. *Inorg. Chem.* **1971**, *10*, 1643.
(22) The melting points of the host–guest adducts were as follows, with the monomer adduct given first and the polymer adduct in parentheses: acrylic acid, 205–222 °C (208–249 °C); acrylic anhydride, 213–223 °C (221–233 °C); acrylonitrile, 235–244 °C (235–246 °C); methyl acrylate, 232–245 °C (231–248 °C); methyl methacrylate, 237–243 °C (239–245 °C); methyl vinyl ketone, 192–231 °C (187–246 °C); acrylonitrile/acrylic acid, 208–229 °C (217–235 °C); acrylonitrile/methyl methacrylate, 231–239 °C (231–248 °C). All the host–guest adducts melted with apparent decomposition.
(23) Brandrup, J., Immergut, E. H. Eds. "Polymer Handbook", 2nd ed.; Wiley-Interscience: New York, 1975.
(24) Allcock, H. R.; Levin, M. L.; Whittle, R. R., submitted for publication in *Inorg. Chem.*
(25) Inoue, Y.; Nishioka, A. *Polym. J.* **1972**, *3*, 149.
(26) Matsuzaki, K.; Kanai, T.; Kawamura, T.; Matsumoto, S.; Uryu, T. *J. Polym. Sci., Polym. Chem. Ed.* **1973**, *11*, 961.
(27) Chapiro, A. "Radiation Chemistry of Polymeric Systems"; Interscience: New York, 1962; p 355.
(28) Peat, I. R.; Reynolds, W. F. *Tetrahedron Lett.* **1972**, *14*, 1359.
(29) Gel permeation chromatography suggested that both the bulk- and clathrate-synthesized poly(methyl methacrylate) had a broad molecular weight distribution with roughly the same dispersity (M_w/M_n = 6.6 and 7.4, respectively). The measurements were carried out with the use of a Waters Associates ALC/GPC 501 chromatograph equipped with one 10^3-Å and two 10^6-Å Polymer Laboratories PL gel columns. Tetrahydrofuran was used as the eluent at a flow rate of 0.5 mL/min and a temperature of 30 °C. Polystyrene standards were used to calibrate the instrument.
(30) Merle-Aubrey, L.; Merle, Y. *Eur. Polym. J.* **1980**, *16*, 227.
(31) Davies, W. G.; Jones, D. P. In "Colloidal and Morphological Behavior of Block and Graft Copolymers"; Molau, G. E., Ed.; Plenum Press: New York, 1971; p 63.

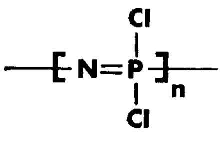
Polymerization and Halogen Scrambling Behavior of Phenyl-Substituted Cyclotriphosphazenes[1]

Harry R. Allcock* and Mark S. Connolly

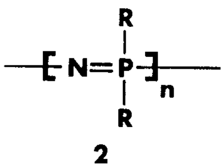
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received June 14, 1984*

ABSTRACT: A new series of poly(organophosphazenes) with phenyl groups bonded to the skeleton has been prepared by the polymerization of phenylhalogenocyclotriphosphazenes. In addition, evidence about the mechanism of chlorophosphazene polymerization has been obtained by halogen scrambling studies. 1-Phenyl-1,3,3,5,5-pentachlorocyclotriphosphazene, $N_3P_3Cl_5Ph$ (**5a**), undergoes a ring-opening thermal polymerization at 250 °C. The resultant high polymer reacts with sodium trifluoroethoxide, sodium phenoxide, or piperidine to yield poly(organophosphazenes) that are free from P–Cl bonds. 1-Phenyl-1-bromo-3,3,5,5-tetrachlorocyclotriphosphazene, $N_3P_3Cl_4BrPh$ (**5b**), also polymerizes at 250 °C but with scrambling of the bromine atoms between different phosphorus sites. The trimer, **5b**, itself undergoes halogen scrambling at temperatures as low as 178 °C. The cyclophosphazenes, **5a** and **5b**, copolymerize at 250 °C with $(NPCl_2)_3$. The copolymerization of **5a** and $N_3P_3Cl_5Me$ provides a method for the synthesis of phosphazene polymers that bear both alkyl and aryl substituent groups. The trimers, **5b** and $N_3P_3Cl_4BrMe$, are accelerators for the polymerization of $(NPCl_2)_3$ at 250 °C, while **5a** and $N_3P_3Cl_5Me$ are weak inhibitors. However, polymers prepared in the presence of these inhibitors had molecular weights similar to those prepared from pure $(NPCl_2)_3$ or in the presence of the accelerators. The mechanistic implications of these results are discussed.

High molecular weight poly(organophosphazenes) of formula $[NP(OR)_2]_n$, $[NP(NHR)_2]_n$, and $[NP(NR_2)_2]_n$ are well-known.[2-9] These polymers are prepared by the interaction of poly(dichlorophosphazene) (**1**) with alkoxides, aryl oxides, or amines. However, because these molecules possess organic side units bonded to phosphorus through oxygen or nitrogen, reaction pathways exist that permit decomposition or depolymerization at temperatures above 250 °C.


$$\left[N=\overset{Cl}{\underset{Cl}{P}}\right]_n$$

1

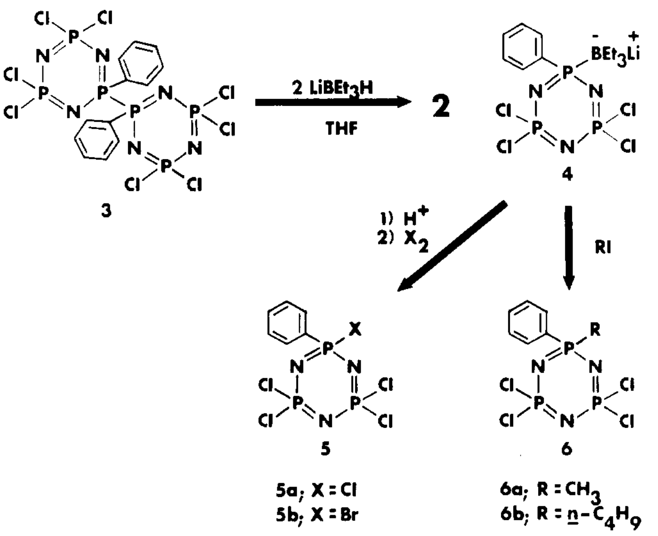

$$\left[N=\overset{R}{\underset{R}{P}}\right]_n$$

2

An approach to enhancing the thermal stability of polyphosphazenes and modifying their physical properties involves the synthesis of derivatives **2** that possess alkyl or aryl groups bonded directly to the skeletal phosphorus atoms. Such macromolecules would be analogues of alkyl- or arylpolysiloxanes. Earlier attempts to prepare such polyphosphazenes by the interaction of **1** with organometallic reagents[10-12] revealed some serious difficulties, since metal–halogen exchange reactions and skeletal cleavage accompanied substitution.[12] However, Neilson and Wisian-Neilson have recently reported a promising condensation–polymerization route that yields poly(alkyl- or alkylarylphosphazenes) of type **2**.[13]

An alternative approach being examined in our laboratory involves the synthesis of cyclotriphosphazenes that bear alkyl or aryl side groups bonded to the ring, and the polymerization of these species to linear polyphosphazenes.[14-18] Recently, we reported the first syntheses of 1-phenyl-1-halotetrachlorocyclotriphosphazenes, $N_3P_3Cl_4X(Ph)$ (**5**), and 1-phenyl-1-al-

Scheme I



kyl-tetrachlorocyclotriphosphazenes, $N_3P_3Cl_4(Ph)(R)$ (**6**).[18] In this paper, we describe the polymerization of these cyclic trimers and their use as initiators for the polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$. In addition, these polymerization reactions provide a new insight into the mechanism of polymerization of halocyclophosphazenes.

Results and Discussion

Synthesis of the Cyclic Trimers. Cyclotriphosphazenes **5** and **6** were synthesized by a new technique reported recently.[18] The method is summarized in Scheme I. It involves the reaction of a bi(cyclotriphosphazene) (**3**) with 2 equiv of $LiBEt_3H$ in THF solvent. Treatment of the intermediate triethylborata-substituted phosphazene anion, **4**, with proton-releasing agents leads to the formation of a hydridocyclophosphazene which, after treatment with excess halogen in CCl_4, gives species **5**. Compounds **5** were prepared in which X was Cl, Br, and I. Alternatively, **4** reacts with excess alkyl halide to give **6** in high yield. Compounds **6** were prepared where R was CH_3, C_2H_5, n-C_3H_7, n-C_4H_9, i-C_3H_7, and $CH_2CH{=}CH_2$.

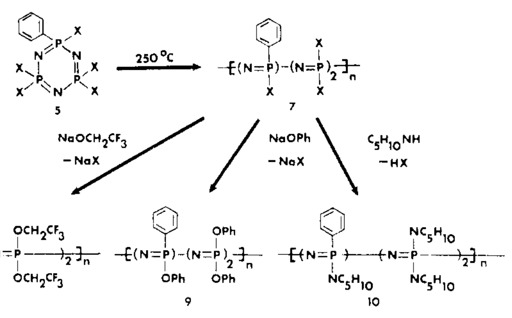
The focus of this polymerization study was on the reactions of species **5**, in which X is Cl and Br, and compounds **6**, in which R is CH_3 and n-C_4H_9. These compounds yielded the most useful mechanistic information.

It should be noted that extensive efforts were made to ensure that the purity of **5** and **6** was uniform before the polymerization experiments were carried out. Failure to do this would alter the results markedly.

Homopolymerization Reactions. Rigorously purified samples of **5** polymerized at 250 °C. This process is depicted in Scheme II. The polymerization of **5b** leads to halogen scrambling, and this will be discussed in a later section.

Marked differences in polymerization behavior were found for the different variants of species **5**. When X was Br (**5b**), the trimer polymerized readily during 4.5–24 h at 250 °C, whereas, when X was Cl (**5a**), longer polymerization times were required (20–56 h). Species **5b** polymerized at 200 °C, and **5a** polymerized at temperatures as low as 225 °C. However, these processes required very long reaction times (26 and 13 days, respectively). Prolonged heating of **5** led to cross-linked polymers. The presence of a bromine atom geminal to the phenyl group in **5** appears to facilitate polymerization. The mechanistic implication of this will be discussed later.

Scheme II



X = Cl or Br, as defined by structures 5a and 5b

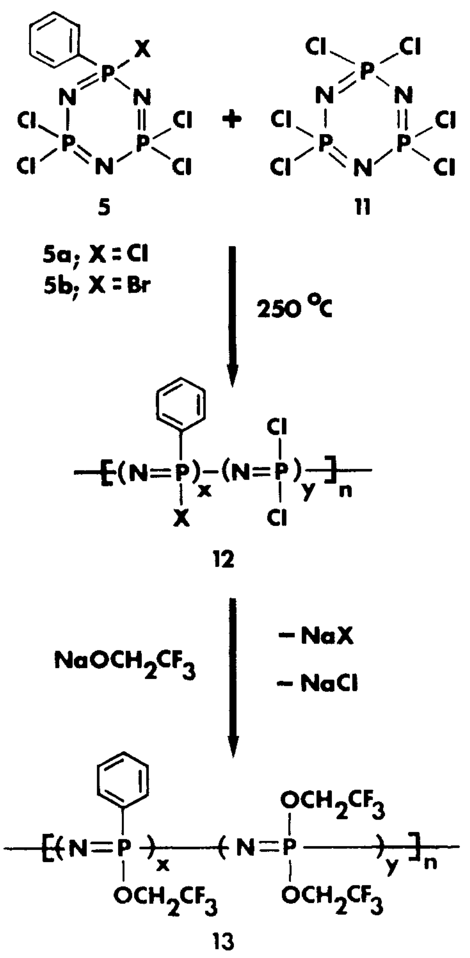
Polyphosphazenes that contain phosphorus–halogen bonds are hydrolytically unstable.[6] Therefore, full characterization of polymers **7** was undertaken only after all the halogen atoms had been replaced by organic residues. Model studies with related cyclotriphosphazenes and bi(cyclophosphazenes) indicated that complete halogen replacement could be expected with the use of trifluoroethoxide ion, phenoxide ion, or piperidine.[1b,14,17] Thus, the various polymers derived from **5** were allowed to react with sodium trifluoroethoxide. The polymer obtained from **5a** was also allowed to react with sodium phenoxide or piperidine. The characterization data for these derivatized polymers are summarized in Tables I and IV.

The general structure of these derivative polymers is shown in **8–10**. These structures were confirmed by ^{31}P NMR and IR spectroscopy and by elemental analysis. The trifluoroethoxy-substituted polymers derived from **5a** and **5b** were found to be identical. Moreover, both of these polymers were similar to an analogous derivative prepared previously via the polymerization of $N_3P_3F_5Ph$, followed by treatment with sodium trifluoroethoxide.[14]

At 250 °C, rigorously purified samples of **6** yielded a broad range of products from oligomers to high polymers. For example, **6a** became severely discolored and only slightly viscous after 24 h at 250 °C. No increase in viscosity was detected even after 22 days at the same temperature. Methyl chloride was identified as a product from these reactions, and this suggests that the P–alkyl bonds cannot survive for long periods of time in the relatively hostile environment needed to bring about ring-opening polymerization.[19] Similar degradative side reactions have been reported earlier for alkylchlorophosphazenes.[17] In the present work, treatment of the reaction products from **6a** with sodium trifluoroethoxide yielded discolored, polymeric species with very broad molecular weight distributions ($10^4 - >10^6$). Similar results were obtained with **6b**. Thus, it appears that the polymerization process is inhibited when two alkyl or aryl side groups are present geminal to each other on the phosphazene ring.[14] Explanations for this can be made in terms of a lowering of the ceiling temperature, steric hindrance to chain propagation, or the generation of inhibitory side products (see later).

Copolymerization Reactions. Cyclotriphosphazenes **5** copolymerized with equimolar amounts of $(NPCl_2)_3$ (**11**) at 250 °C (Scheme III). The rate of copolymerization was faster when X was Br than when X was Cl. Halogen scrambling was detected in the formation of the copolymer derived from **5b**. Therefore, structure **12** is an oversimplified representation. The incorporation of P–Ph units into the copolymer was deduced from ^{31}P NMR spectroscopy and from elemental analyses (Table IV) of the derivative polymer **13**. The results suggested tentatively that the copolymerization reactivity of **5a** was similar to that of $(NPCl_2)_3$ and the reactivity of **5b** is greater than that of $(NPCl_2)_3$.

Scheme III



Compound **5a** also copolymerized with an equimolar amount of $N_3P_3Cl_5Me$ (**14**) during 29.5 h to yield a polymer (**15**) that contained both methyl and phenyl side groups linked to the skeleton (Scheme IV). After replacement of the chlorine atoms by trifluoroethoxy groups to give **16**, the copolymer was found to contain 10.0% methyl and 5.8% phenyl substituents (based on ^{31}P NMR and elemental analyses). These data are summarized in Tables I and IV. Thus, the methyl-substituted trimer appears to be more reactive in copolymerization than does **5a**. This agrees with the faster homopolymerization behavior[17] of **14** and could reflect the influence of side-group steric hindrance on chain propagation.

Copolymerization of **6** with $(NPCl_2)_3$, followed by treatment with sodium trifluoroethoxide, yielded discolored, polymeric materials that had broad molecular weight distributions (10^5–$>10^6$). These species were similar to the products obtained from the analogous homopolymerization reactions and support the belief that the presence of two geminal alkyl or aryl units on a phosphazene ring inhibits the polymerization process.

Characterization and Properties of the Organo-Substituted Polymers. All the organo-substituted polymers and copolymers derived from **5** were characterized by a combination of ^{31}P NMR and IR spectroscopy, elemental analysis, gel permeation chromatography (GPC), and differential scanning calorimetry. These data are summarized in Tables I and IV and in the Experimental Section.

Scheme IV

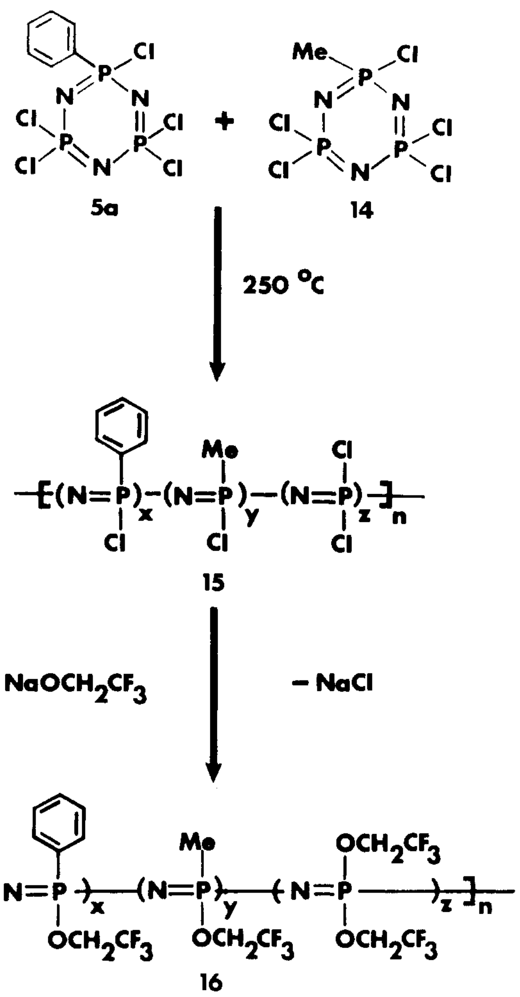


Table I
Polymer ^{31}P NMR Data (Organo Substituted)[a]

polymer	chemical shifts, ppm	
	$P(R)(OR')$	$P(OR')_2$
$—[N{=}P(OCH_2CF_3)_x(C_6H_5)_y]_n—$ (**8**, **13**)	+5.6[b]	−8.2[a]
$—[N{=}P(OC_6H_5)_{1.67}(C_6H_5)_{0.33}]_n—$ (**9**)	−3.3	−19.6
$—[N{=}P(NC_5H_{10})_{1.67}(C_6H_5)_{0.33}]_n—$ (**10**)	−6.3	−6.3
$—[N{=}P(OCH_2CF_3)_{1.68}(CH_3)_{0.20}$-$(C_6H_5)_{0.12}]_n—$ (**16**)	+19.3[c] +6.1[c]	−7.4

[a] The assignments are based on comparisons with the respective homopolymers and on the relative peak areas. [b] These values were virtually identical for the homopolymers derived from **5a** (x = 1.67, y = 0.33), the homopolymers derived from **5b** (x = 1.67, y = 0.33), the 1:1 copolymer derived from **5a** and $(NPCl_2)_3$ (x = 1.83, y = 0.17), and the 1:1 copolymer derived from **5b** and $(NPCl_2)_3$ (x = 1.80, y = 0.20). [c] The assignment of these resonances was as follows: $P(CH_3)(OCH_2CF_3)$: +19.3 ppm; $P(C_6H_5)(OCH_2CF_3)$: +6.1 ppm.

The infrared spectra (Experimental Section) were compatible with a structure such as **8**, **9**, or **10**. An intense absorption was detected between 1200 and 1300 cm^{-1}, which is characteristic of the —P=N— skeleton.[6] The spectra also showed characteristic absorptions for alkyl or aryl groups and for the respective organic cosubstituent groups (OCH_2CF_3, OC_6H_5, or NC_5H_{10}).

The ^{31}P NMR spectra of the derivatized polymers (Table I) contained two broad areas of resonance. The first appeared between +19.3 and −6.3 ppm and was assigned to P(R)(OR′) nuclei. The second appeared upfield between −6.3 and −19.6 ppm and was assigned to $P(OR')_2$ nuclei. For the polymers prepared via the homopolymerization of **5**, the ratio of these two units (as measured by integration of the areas under the two envelopes) was 1:2. The

Table II
Polymer ^{31}P NMR Data (Halogen Substituted)

polymer structure	cyclophosphazene "monomer(s)"	chemical shift, ppm	resonance assignt
$-[N{=}P(Cl)_{1.67}(C_6H_5)_{0.33}]_n-$	$N_3P_3Cl_5Ph$ (**5a**)	-0.3^a	P(Ph)Cl
		-19.5^a	PCl_2
$-[N{=}P(Cl)_x(Br)_y(C_6H_5)_z]_n-$ $(x + y + z = 2)$	$N_3P_3Cl_4Br(Ph)$ (**5b**)	-1.5^b	P(Ph)Cl
		-19.8^b	$P(Ph)Br + PCl_2$
		-48.5^b	PClBr
		$-79.6^{b,c}$	PBr_2
$-[N{=}P(Cl)_x(Br)_y(CH_3)_z]_n-$ $(x + y + z = 2)$	$N_3P_3Cl_4Br(CH_3)$	$+10.3^b$	P(Me)Cl
		-8.1^b	P(Me)Br
		-20.4^b	PCl_2
		-48.9^b	PClBr
		$-79.6^{b,c}$	PBr_2
$-[N{=}P(Cl)_{1.68}(CH_3)_{0.20}(C_6H_5)_{0.12}]_n-$	**5a** and $N_3P_3Cl_5Me$	$+11.8^a$	P(Me)Cl
		-1.2^a	P(Ph)Cl
		-20.3^a	PCl_2
$-[N{=}PBr_2]_n-$	$N_3P_3Br_6$	-79.5^b	PBr_2
$-[N{=}P(Cl)_x(Br)_y]_n-$ $(x + y = 2)$	$N_3P_3Cl_6$ and $N_3P_3Br_6$	-19.5^b	PCl_2
		-47.5^b	PClBr
		-79.3^b	PBr_2

[a] Values are for samples in THF. [b] Values for samples in toluene. [c] These values are approximate due to the small area under the resonances.

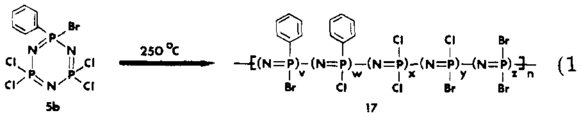
ratios of the different units in the copolymers formed from 5 and other trimers were measured in the same way. These ratios depended on the relative concentrations of the trimers in the initial mixture (see Table IV and Experimental Section). Elemental analyses were used to confirm the various repeating unit ratios.

The trifluoroethoxy- and phenoxy-substituted polymers are elastomers. Presumably, this property is due to the presence of the bulky phenyl groups which disrupt the chain symmetry and retard microcrystallite formation. By contrast, the homopolymers, $[NP(OCH_2CF_3)_2]_n$ and $[NP(OPh)_2]_n$, are microcrystalline, film- and fiber-forming macromolecules.[2,3] The piperidino-substituted polymer is a brittle, film-forming material.

The polymers had GPC average molecular weights of 1×10^6 or higher (Table IV).

The glass transition temperatures (T_g) for the organo-substituted polymers and copolymers are listed in Table IV. The values for 8–10 were found to be 18–56 °C higher than those of the related *homo*polymers $[NP(OCH_2CF_3)_2]_n$ (T_g = −66 °C), $[NP(OC_6H_5)_2]_n$ (T_g = −8 °C), and $[NP(NC_5H_{10})_2]_n$ (T_g = +19 °C).[3,5,6] This reflects the influence of the bulky phenyl substituent on the torsional mobility of the polymer backbone. Polymers 8 derived from **5a** and **5b** had nearly identical T_g values. Similar results were obtained for copolymers 13. Interestingly, the T_g value for 16 was almost identical with those recorded for 8 and $[NP(OCH_2CF_3)_{1.67}(CH_3)_{0.33}]_n$ (T_g = −50 °C).[17] Apparently the *presence* of a cosubstituent group on the average every three repeat units along the polymer chain is more important than its size with respect to influencing the chain flexibility.

Structure of the Polymer Derived from 5b. As described, samples of rigorously purified **5b** in the molten state at 250 °C undergo a slow viscosity increase over a period of several hours. If polymerization is allowed to proceed until the reaction mixture is almost completely immobile, an approximately 88% conversion of **5b** to polymer 17 is obtained, as measured by ^{31}P NMR techniques (eq 1).



(1)

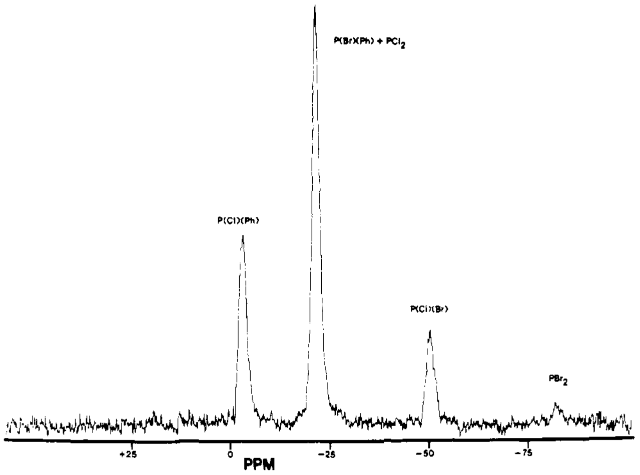


Figure 1. ^{31}P NMR spectrum of the poly(halogenophosphazene) derived from $N_3P_3Cl_4Br(Ph)$, **5b**, in toluene solution.

The ^{31}P NMR spectrum of this polymer in toluene contained resonances at −1.5, −19.8, −48.5, and ca. −79.6 ppm (Figure 1).[20] This contrasted with the ^{31}P NMR spectrum of the polymer derived from **5a**, for which resonances were detected only at −0.3 (33%) and −19.5 (67%) ppm (in THF). These latter resonances correspond to P(Ph)Cl and PCl_2 groups, respectively. Thus, the spectrum of the polymer from **5b** was compatible with a structure in which exchange of halogen atoms had occurred among the several different phosphorus atom environments. The assignments for the different resonances are summarized in Table II, and the logic behind these assignments is as follows.

First, the resonances for 17 at −1.5 and −19.8 ppm were assigned to P(Ph)Cl and PCl_2 units, respectively, by comparison with the spectra of the homopolymers derived from **5a** and $(NPCl_2)_3$.

Second, the P(Ph)Br resonance was identified by comparison with the spectrum of a polymer obtained by the polymerization of $N_3P_3Cl_4BrMe$. The ^{31}P NMR spectrum of this polymer showed resonances at +10.3, −8.1, −20.4, −48.9, and ca. −79.6 ppm (Table II).[20] Results reported previously[17] for a polymer derived from $N_3P_3Cl_5Me$ suggested that the resonances at +10.3 and −20.4 ppm could be assigned to P(Me)Cl and PCl_2 units, respectively.

Therefore, the resonance at −8.1 ppm was attributed to P(Me)Br units. This indicated that the chemical shift for this phosphorus atom is shifted upfield by 18.4 ppm when chlorine is replaced by bromine. If a similar shift occurs in the phenylbromochlorophosphazene polymer (**17**), then the P(Ph)Br resonance should appear at ca. −19.9 ppm. This resonance would be hidden beneath the PCl_2 resonance at −19.8 ppm. Thus, the observed resonance at −19.8 ppm probably includes those from both the PCl_2 and P(Ph)Br units.

Third, the resonance at −79.6 ppm from **17** was assigned to PBr_2 units. This resonance would be expected to be furthest upfield, a consequence of the high shielding of the phosphorus atoms by two bromine atoms. Furthermore, statistically this resonance would be expected to be the weakest in the spectrum because of the low probability of replacement of two chlorine atoms on the same phosphorus by bromine.

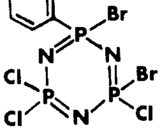
However, additional evidence for this assignment was obtained by the preparation and study of the homopolymer, $(NPBr_2)_n$. A rigorously purified sample of $(NPBr_2)_3$ was polymerized at 220 °C. This polymer was swelled by, but did not dissolve in, toluene. It showed a singlet in the ^{31}P NMR spectrum at −79.5 ppm (PBr_2) after the trimer $(NPBr_2)_3$ (−44.2 ppm) and tetramer $(NPBr_2)_4$ (−69.8 ppm) had been removed by extraction with hot toluene.

Fourth, the resonance at −48.5 ppm from **17** was assigned to PClBr units. This was based on the spectrum obtained from a 1:1 copolymer prepared by heating $(NPCl_2)_3$ and $(NPBr_2)_3$ at 220 °C. This copolymer was insoluble in, but was swelled by, toluene. After removal of cyclic species by extraction with hot toluene, the polymer showed resonances at −19.5 (PCl_2), −47.5 (PClBr), and −79.3 (PBr_2) ppm.[20]

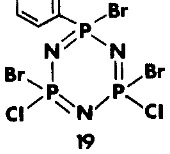
Fifth, to confirm that the assigned resonances were associated with polymer **17** and not with oligomeric impurities, a concentrated solution of the polymer was reprecipitated from toluene into dry hexane. The integrated areas and peak positions were identical (within the experimental error of the NMR instrument) before and after reprecipitation.

Halogen Scrambling Reactions. The mechanism of the thermal ring-opening polymerizations of halogenocyclophosphazenes is believed to involve the ionization of halide ion from phosphorus.[6,21] The main evidence for this was based on dielectric constant and electrical conductance changes detected in molten $(NPCl_2)_3$ as the temperature was varied.[22] Very little additional evidence for this mechanism has appeared in the last 20 years, even though it is a key concept for the polymerization chemistry of these systems. The thermal behavior of **5b** provides some important additional evidence.

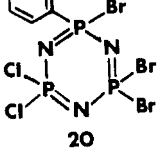
As discussed, the conversion of **5b** to its high polymer is accompanied by halogen migration from one repeating unit to another. Moreover, new cyclic trimeric phosphazenes such as **5a** and *non-gem*-$N_3P_3Cl_3Br_2Ph$ (**18**) are formed by halogen migration processes, with the formation of **5a** being the predominant reaction.[23] These cyclic products were identified by ^{31}P NMR, gas chromatography, and mass-spectrometric techniques.[24] No P–C bond cleavage was detected, although discoloration was noted for some systems that could indicate organic side-group decomposition. This aspect will be discussed later.



18

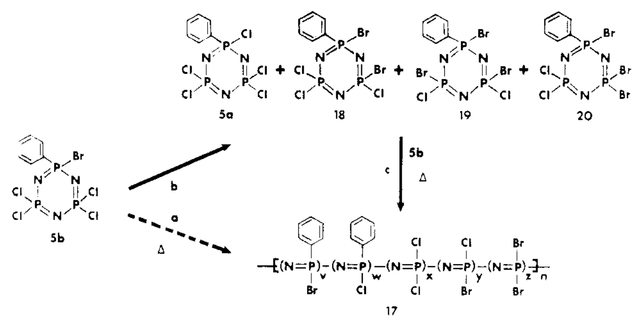


19



20

Scheme V



Halogen scrambling was also detected when **5b** was heated at temperatures that were insufficient to promote polymerization. For example, no polymer was formed (based on ^{31}P NMR evidence) when **5b** was heated at 178 °C for 72 h. However, ^{31}P NMR resonances were detected that corresponded to **5a** (12%), **5b** (85%), and **18** (3%). These conclusions were confirmed by the results of gas chromatography/mass-spectrometric experiments (GC/MS). The formation of **18** must result from the interaction of two molecules of **5b** to give one molecule of **5a** and one molecule of **18**. However, the product ratio of **5a** and **18** always deviated from the expected 1:1 molar ratio. Therefore, it is speculated that **18** decomposes under the reaction conditions (and is a source of discoloration of the molten reaction mixture).

Halogen migration within the trimer population was also detected under conditions that brought about the initial appearance of high polymer. For example, after 72 h at 182 °C, species **5b** yielded ∼3% high polymer, as well as **5a** (34%), **5b** (56%), and **18** (9%), as deduced by a combination of ^{31}P NMR and gas chromatography analyses. Moreover, a new cyclotriphosphazene (∼1%) was detected by GC/MS techniques and was tentatively assigned the structure **19**. This assignment was based on the chemical ionization mass spectrum (see Experimental Section), and on the assumed greater likelihood that a PCl_2 unit in **18** would undergo halogen exchange with Br (from another molecule) to give **19** than a PClBr unit would undergo a similar reaction to yield **20**. No PBr_2 units were detected among the cyclic species, but the possibility exists that these might be present at concentrations too low to be detected by the ^{31}P NMR method.

Temperature has a strong influence on these halogen exchange reactions. It also has a profound effect on the polymerization process. The polymerization of **5b** at 250 °C requires <24 h for completion. At 200 °C, it requires 26 days.

In view of these observations, the following question needs to be answered Does the halogen migration detected in polymer **17** result from halogen exchange before, during, or after polymerization of **5b**? Our results are compatible with the idea that most of the halogen scrambling occurs before polymerization of the trimers (Scheme V). Thus, **17** is, in fact, a copolymer of **5b** with **5a**, **18**, and possibly **19** and **20** (via pathways b and c of Scheme V). In these terms, the P(Ph)Cl group in **17** is derived from **5a**, the PClBr groups from **18** or **19**, and so on. The detection of PBr_2 resonances in the ^{31}P NMR spectra of **17** could be construed as evidence of the prior formation of **20**. The evidence that halogen scrambling occurs mainly at the trimer stage is as follows.

First, sealed tubes of **5b** were heated at 250 °C and were analyzed by ^{31}P NMR techniques after 2-, 4-, 6-, and 9-h

Table III
^{31}P NMR Analysis of the Cyclotriphosphazenes and Polyphosphazenes Present during the Polymerization of 5b

time, h	% of reactn mixture	resonance obsd[a]	integrated area, %
		(a) Cyclotriphosphazenes	
0	100	P(Ph)Cl	0
		PCl_2	67
		P(Ph)Br	33
		PClBr	0
2	89	P(Ph)Cl	5
		PCl_2	66
		P(Ph)Br	27
		PClBr	2
4	39	P(Ph)Cl	11
		PCl_2	61
		P(Ph)Br	22
		PClBr	6
6	25	P(Ph)Cl	21
		PCl_2	59
		P(Ph)Br	10
		PClBr	10
9	12	P(Ph)Cl	33
		PCl_2	50
		P(Ph)Br	0
		PClBr	17
		(b) Polyphosphazenes	
0	0	P(Ph)Cl	0
		P(Ph)Br + PCl_2	0
		PClBr	0
		PBr_2	0
2	11	P(Ph)Cl	0
		P(Ph)Br + PCl_2	100
		PClBr	0
		PBr_2	0
4	61	P(Ph)Cl	21
		P(Ph)Br + PCl_2	69
		PClBr	8
		PBr_2	2
6	75	P(Ph)Cl	22
		P(Ph)Br + PCl_2	63
		PClBr	10
		PBr_2	5
9	88	P(Ph)Cl	25
		P(Ph)Br + PCl_2	11
		PClBr	11
		PBr_2	3

[a] The ^{31}P NMR resonances were assigned as follows: P(Ph)Cl, 28.5 (t), J_{PNP} = 15.1; PCl_2, 20.6 (d), J_{PNP} = 8.2; P(Ph)Br, 14.8 (t) ppm, J_{PNP} = 8.2 Hz; PClBr, ca. −5.4 (m) ppm, coupling unresolved. The P(Ph)Cl resonance was attributed to **5a**, while the P(Ph)Br resonance indicated the presence of **5b**. The resonances at ca. −5.4 ppm were assigned[6] to PClBr, and corresponded to **18**. All values were for samples in toluene. [b] The observed chemical shifts for these resonances are listed in Table II.

reaction (which corresponded to 11%, 61%, 75%, and 88% conversion to polymer **17**). The integrated peak areas for all resonances are listed in Table III. The high polymer formed initially (2 h, 11%) gave no resonances that corresponded to halogen-scrambled products. The cyclophosphazenes had undergone only a small amount of halogen scrambling at this stage.[25] Specifically, the species present were **5b** (77%), **5a** (19%), and **18** (4%), as determined by a combination of ^{31}P NMR and gas-chromatographic techniques.[26]

By the time that a 61% conversion to polymer **17** had occurred, a significant amount of halogen scrambling was detected for both the cyclic and polymeric species. At the 88% conversion stage (the practical limit for reproducible polymerization because of the high viscosity), the trimeric product consisted mainly of **5a**, a result that is compatible with the slow polymerization character of this compound. Species **5b** could not be detected by ^{31}P NMR methods, but small amounts of **5b** and **18** were detected by gas chromatography. Significantly, the ratio of the different repeating units in the final form of polymer **17** was virtually identical with that found for the polymer formed during intermediate stages of the polymerization reaction. Moreover, prolonged heating of **17** to bring about cross-linking did not alter the composition significantly. This favors the view that most of the polymer was formed from a mixture of halogen-scrambled trimers that provided PCl_2, PClBr, PBr_2, P(Ph)Cl, and P(Ph)Br units.

Second, the heating of excess **5b** with poly(dichlorophosphazene), $(NPCl_2)_n$, at 182 °C for 72 h yielded a final polymer that contained less than 5% PClBr units (by ^{31}P NMR spectroscopy). However, under these conditions, **5b** underwent halogen scrambling to give **5a** (49%), unreacted **5b** (36%), **18** (12%), and the product tentatively identified as **19** (3%). Thus, it appears that trimer–trimer halogen scrambling is faster than halogen scrambling between trimer and polymer.

Third, polymer **17** was heated at 182 °C for 72 h with excess **5a**. After this treatment, the polymer resonance from PBr_2 units had disappeared, the PClBr resonance had decreased by 7%, PCl_2 + P(Ph)Br had increased by 9%, and P(Ph)Cl had increased by 1%. More significantly, the cyclotriphosphazene product mixture was found to consist of **5b** (6%), **18** (0.2%), and unreacted **5a** (94%) (based on ^{31}P NMR and gas chromatography). Thus, some halogen exchange can take place between trimeric and polymeric species, but it does not appear to be an important factor in determining the composition of polymer **17**, although it may account for the presence of residual **5b** and some **18** following the polymerization of **5b**.

Thus, the final composition of **17** (Scheme V) appears to be mainly a consequence of copolymerization between halogen-scrambled trimers rather than a result of trimer–polymer halogen scrambling in the later stages of the polymerization reaction. More interesting, but yet unproved, is the possibility that the halogen exchange process is an integral part of the initiation or chain propagation processes (see the following section).

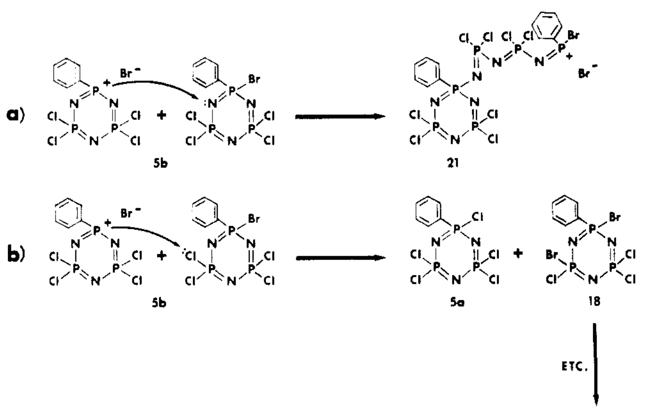
It should be noted that halogen exchange at phosphorus is a facile process in other systems also. Mixtures of PCl_3 and PBr_3 undergo essentially random halogen exchange at temperatures below 100 °C.[27] Other tri- and tetracoordinate phosphorus halide systems behave in the same way.[28-30]

Influence of Other Trimers on $(NPCl_2)_3$ Polymerization. The bromocyclophosphazene **5b** polymerizes at a faster rate than its chloro analogue, **5a**. Hence, it was of interest to examine the influence of **5b** on the polymerization of $(NPCl_2)_3$. When samples of $(NPCl_2)_3$ were heated at 250 °C in the presence of 1.0 mol % **5b** or $N_3P_3Cl_4BrMe$, the polymerization rate was quadrupled. After treatment with sodium trifluoroethoxide to replace the chlorine and bromine atoms, the resultant polymers were indistinguishable from those prepared in the absence of the bromophosphazene. On the other hand, species **5a** or $N_3P_3Cl_5Me$ in 1.0 mol % concentration slightly retarded the rate of polymerization of $(NPCl_2)_3$.

The role of **5b** or $N_3P_3Cl_4BrMe$ as accelerators can be understood in the same terms as those described for their "homopolymerization" reactions. However, it was necessary to determine if this effect was due to the liberation of molecular bromine. It was found that 1.0 mol % of dry Br_2 retarded the polymerization of $(NPCl_2)_3$.[31,32]

Polymerization Mechanism. We suggest that the cleavage of a P–Br bond is an integral part of both the initiation (mechanism a) and halogen exchange processes (mechanism b), as illustrated in Scheme VI. The cleavage

Scheme VI



is depicted as heterolytic, but a homolytic cleavage process cannot be ruled out when bromine is involved.

As shown experimentally, the polymerization of **5b** is faster than that of **5a**. Moreover, in the polymerization of **5b**, the combined influences of halogen exchange and polymerization have the effect of concentrating bromine in the polymer rather than in the unpolymerized trimers. Hence the view that the P–Br bonds are associated with the polymerization process appears to be sound. Phosphorus–bromine bonds are weaker (to homolytic cleavage) than are phosphorus–chlorine bonds,[33] but the relative propensity for ionization in a medium of molten phosphazene is not known. Hence, the question of a free radical vs. an ionic initiation process cannot be settled from the present data.

In the absence of more definitive facts, we assume that species **21** begins the chain propagation process. The ease of attack by species of type **21** on another trimer molecule should depend on steric hindrance effects at the growing chain end. A phenyl group at the chain end would be expected to bring about some retardation, but the effect would be more serious when two organic groups occupied and terminal site. This may explain why **6a** and **6b** do not yield exclusively high polymers. Another contributing factor may be strong electron supply from the terminal organic side units into the cationic phosphorus center. The fact that halogen exchange between trimers occurs at temperatures below those at which polymerization takes place provides additional evidence that chain *propagation* may be the slow step in this mechanism. Eventual chain branching or cross-linking could occur following thermal cleavage of P–halogen bonds from middle units.

Experimental Section

Materials. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, kindly supplied by The Firestone Tire and Rubber Co., was purified by two fractional sublimations at 0.05 torr. Hexabromocyclotriphosphazene, $(NPBr_2)_3$ (Alfa Ventron, 90%), was purified by three recrystallizations from heptane and three sublimations at 0.05 torr. The Grignard reagents (Alfa Ventron), $LiBEt_3H$ (Aldrich, 1.0 M solution in THF), alkyl halides (Aldrich), sodium spheres (Aldrich), tribromomethane (Aldrich), and phenol (Baker) were commercial products and were used as received. The copper complex, $[n\text{-}Bu_3PCuI]_4$, was prepared as reported in the literature.[34] Tetrahydrofuran (THF) (Curtin Matheson), 1,4-dioxane (Curtin Matheson), toluene, and hexane were distilled into the reaction flask under an atmosphere of dry nitrogen from a sodium benzophenone ketyl drying agent. Tetrachloromethane was distilled in a similar manner from phosphorus pentoxide, while piperidine (Aldrich) and heptane were distilled from calcium hydride. Trifluoroethanol (Halocarbon Corp.) was dried over 3-Å molecular sieves before use. The bromine (Aldrich 99.998%) was either used as received or purified further by distillation. This was accomplished by cooling bromine ($\simeq$25 mL) in a round-bottom flask by means of liquid nitrogen and allowing the bromine to warm to room temperature slowly and distill through a U-tube connected to another round-bottom flask cooled in liquid nitrogen. This procedure was performed under an atmosphere of dry nitrogen. The chlorine gas (Curtin Matheson, UHP) was passed through a trap cooled to −23 °C with a bath of dry ice and *o*-dichlorobenzene. Solvents used for gel permeation chromatography and precipitations of poly(organophosphazenes) were used as received. Precipitations of poly(halophosphazenes) were performed with the use of dry solvents. All manipulations and syntheses of poly(halophosphazenes) were carried out under an atmosphere of dry nitrogen using standard Schlenk or drybox techniques.

Equipment. ^{31}P NMR spectra were recorded on a Varian CFT-20 spectrometer operating at 32 MHz in the Fourier transform mode. The data were processed by using the computer contained within the CFT-20 spectrometer. Positive chemical shifts were downfield from external 85% phosphoric acid. A 45° flip angle was employed in the Fourier transform data collection. To determine the peak integration areas, a pulse repetition rate of 15 s for halogen-substituted polymers and 30 s for halogen-substituted cyclic trimers was employed. Under these conditions, the integrated areas were accurate to ±3%. For cyclic and polymeric phosphazenes with organic side units, a 3-s pulse repetition rate was sufficient for ±3% accuracy. ^1H NMR spectra were recorded on a Bruker WP-200 spectrometer operating at 200 MHz in the Fourier transform mode. The data were processed by using the computer contained within the WP-200 spectrometer. Positive chemical shifts were downfield from tetramethylsilane. Infrared spectra were recorded on a Perkin-Elmer 281B or 283B infrared spectrometer. Samples were in the form of films cast on NaCl plates. Microanalyses were obtained by Galbraith Labs. Inc., Knoxville, TN.

Gel permeation chromatograms were obtained with the use of a Waters Associates ALC/GPC 501 instrument fitted with a refractive index detector. Sample concentrations were 1.0% by weight. Acetone was used as the eluent for all trifluoroethoxy-substituted polymers, and THF was used as the eluent for all phenoxy-substituted polymers. The columns consisted of Corning porous glass beads with four 2-ft lengths of $^3/_8$ in. wide sections containing 75, 175, 700, and 2000 Å of stationary phase. Typical analyses were conducted with 2× attenuation, positive polarity, 100–300 psi pressure, and 2.90–2.92 mL/min flow rate. The instrument was calibrated with narrow molecular weight polystyrene standards (Waters Associates) by using THF as the eluent. Thus, molecular weight values for these polyphosphazenes are considered to be approximate.

Gas chromatography was performed with the use of a Varian Model 3700 gas chromatograph using a flame ionization (H_2/air) detector. The stationary phase was 3.0% OV-101 on Chromosorb W-HP (2 m of 80/100 mesh) to detect cyclic phosphazenes, or Chromosorb 102 (2 m of 80/100 mesh) to detect low molecular weight byproducts. The integrated peak areas were determined from the product of the height of the peak at the midpoint of the base and the width at half-height. An analysis of the peak areas from a standard sample composed of **5a** and **5b** indicated that the response of the detector was proportional to the molecular weight of the components. Gas chromatography/mass spectrometry (GC/MS) data (chemical ionization with the use of methane as a carrier gas) were obtained with the use of a Finnegan 3200 mass spectrometer/gas chromatograph. The data were analyzed with the use of a Finnigan 6000 data system.

Glass transition temperatures were recorded with the use of a Du Pont 1090 thermal analyzer with a 910 differential scanning calorimeter. The data were recorded for samples (ca. 10–20 mg) in crimped aluminum pans, with a heating rate of 20 °C/min and a nitrogen flow rate of 30 mL/min. The instrument was calibrated with a mercury standard (T_f = −38.9 °C).

Synthesis of 5, 6, $N_3P_3Cl_5Me$, and $N_3P_3Cl_4BrMe$. These compounds were prepared by synthetic techniques described previously.[16,18]

Polymerization Technique. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$, was purified immediately before polymerization by an additional sublimation at 0.05 torr. The cyclotriphosphazenes **5** and **6** were purified for polymerization by three recrystallizations from pentane or hexane, respectively, followed by five vacuum sublimations at 0.05 torr. Their purity was confirmed by ^{1}H NMR spectroscopy.

The polymerization tubes, Pyrex glass, ca. 170 mm long, ca. 12 mm wide, ca. 8 mm inside diameter, ca. 2 mm wall thickness, with a constriction ca. 30 mm long and 30 mm from the open end, were soaked in "Micro" (International Products, Corp.) cleaning solution for 24 h, followed by five washings each with tap water, distilled water, and distilled/deionized water. The tubes were then dried in an oven at 130 °C for 24 h and were subsequently cooled to room temperature in a desiccator charged with activated silica gel. The tubes were filled with the appropriate trimer, were attached to a vacuum line, and were evacuated for 1 h, after which time the pressure in the system was 0.05–0.02 torr. The tubes were sealed off at the constriction, were wrapped in aluminum wire screen, and were placed on a rocking device in a Freas thermoregulated oven preheated to the desired temperature. They were removed from the oven when the viscosity of the molten reaction mixture was very high, and the mixture was almost imobile. The tubes were then allowed to cool to room temperature, opened in a nitrogen-filled glovebag and, unless stated otherwise, the entire contents (cyclic and polymeric species) were then transferred to the reaction flask for subsequent analysis and/or replacement of the phosphorus–halogen linkages.

Polymerization of 5. These compounds, purified and charged into polymer tubes as described above, were heated at 250 °C. Reaction times varied from 4.5–24 h for **5b** to 20–56 h for **5a**. Discoloration of the reaction products also varied from light yellow for **5b** to light brown for **5a**. However, any discoloration of the reaction products was subsequently removed after the precipitation procedure. Typical conversions to polymer were 76% for **5a** and 86% for **5b**, as determined by ^{31}P NMR analysis of the reaction products. **5a** was also found to polymerize at 225 °C, and **5b** polymerized at 200 °C; however, the reaction times (13 days and 26 days, respectively) were considerably longer. The polymers appeared to be identical with those prepared at 250 °C.

Reaction of 7 with Sodium Trifluoroethoxide. The high polymers, **7**, prepared from **5** were allowed to react with sodium trifluoroethoxide to replace the hydrolytically unstable phosphorus–halogen bonds. The following is a typical procedure. The adhesive, elastomeric contents of the polymerization tube that contained polymer **7**, derived from **5a** (2.45 g, 6.29 mol), were dissolved in THF (50 mL) and filtered under nitrogen to remove any glass fragments. (The polymeric products derived from **5b** were dissolved in toluene because the P–Br linkages were suspected to react with THF). The polymer solution was added dropwise over 30 min to a solution of sodium trifluoroethoxide (3 equiv per P–X bond) prepared from sodium (2.18 g, 0.095 mol) and trifluoroethanol (12.4 g, 0.124 mol) in THF (150 mL). When the addition was complete, the solution was heated to reflux for 72 h. After this time, the solution was allowed to cool to room temperature, was concentrated to ca. 25 mL, and was poured into aqueous HCl (0.05%, 1800 mL). (The concentrated solution of products derived from **5b** was poured into hexane (1800 mL) initially because of the toluene present.) The polymer which precipitated from this solution was filtered off, washed with distilled/deionized water, dissolved in a minimum of THF, and precipitated into distilled/deionized water (1800 mL). Two further precipitations of polymer **8** from THF into hexane (1800 mL) gave the product as a white elastomer (0.89 g, 26%). The polymers **8** derived from **5a** or **5b** were identical after derivatization with sodium trifluoroethoxide. Characterization data are listed in Tables I and IV. The infrared spectrum of $[NP(OCH_2CF_3)_{1.67}(C_6H_3)_{0.33}]_n$ (**8**) contained the following peaks (cm^{-1}): 2950 m, 2880 w (ν_{CH}); 1410 m (ν_{POC}); 1275 vs, 1235 s (ν_{PN}); 1165 vs (ν_{PO}); 1075 vs (ν_{CO}); 995 s (ν_{PO}); 865 m (ν_{POC}); 740 m, 685 m (ν_{aryl}).

Reaction of 7 with Sodium Phenoxide. Polymer **7**, derived from **5a** (2.68 g, 6.82 mmol), was allowed to react with excess sodium phenoxide, prepared from sodium (2.4 g, 0.10 mol) and phenol (13.5 g, 0.14 mol), in a manner similar to that described above for the reactions with sodium trifluoroethoxide. However, this substitution used a solvent system of 1,4-dioxane at reflux to ensure complete substitution of all the P–Cl linkages. Purification of polymer **9** by reprecipitation, as described above, gave an off-white, elastomeric material (2.3 g, 66%). Characterization data are listed in Tables I and IV. The infrared spectrum of $[NP(OC_6H_5)_{1.67}(C_6H_5)_{0.33}]_n$ (**9**) contained the following peaks (cm^{-1}): 3070 w (ν_{CH}); 1595 m, 1490 s ($\nu_{C=C}$); 1225 s (ν_{PN}); 1185 vs (ν_{PO}); 920 vs (ν_{PO}); 750 s, 670 s (ν_{aryl}).

Reaction of Polymer 7 with Piperidine. Polymer **7**, derived from **5a** (2.48 g, 6.37 mmol), was allowed to react with excess piperidine (15.5 mL, 0.16 mol) in THF (250 mL) at reflux for 72 h. After this time, the solution was cooled to room temperature, was concentrated, and was poured into ethanol (95%, 1800 mL). The polymer which precipitated from this solution was recovered by filtration, was dissolved in a minimum of THF, and precipitated into hexane (1800 mL). Further purification by precipitations from THF into 95% ethanol and THF into hexane gave polymer **10** as a white, brittle, film-forming material (1.2 g, 39%). Characterization data are listed in Tables I and IV. The infrared spectrum of $[N{=}P(NC_5H_{10})_{1.67}(C_6H_5)_{0.33}]_n$ (**10**) contained the following peaks (cm^{-1}): 2940 s, 2850 m (ν_{CH}); 1235 s (ν_{PN}); 1185 vs, 1145 m, 1100 s, 1045 s (ν_{CN}); 935 s (ν_{PN}); 795 w, 700 m, 680 m (ν_{aryl}).

Polymerization of 6. These compounds, purified and charged into polymerization tubes as described above, were heated at 250 °C. The contents of the tubes discolored quickly and never yielded highly viscous products, even after heating **6a** for 22 days and **6b** for 32 h. Each sample was derivatized with sodium trifluoroethoxide and was isolated by reprecipitation, as described above. Both products were recovered as discolored, slightly adhesive elastomers. Characterization data are listed in Table IV. The ^{31}P NMR spectrum of "$[NP(OCH_2CF_3)_{1.34}(CH_3)_{0.33}(C_6H_5)_{0.33}]_n$" contained broad resonances at +17.1 (31), +3.5 (24), and −9.8 (45%) ppm, while the infrared spectrum showed the following peaks (cm^{-1}): 2965 m, 2900 w (ν_{CH}); 1420 s (ν_{POC}); 1280 vs, 1220 vs (ν_{PN}); 1150 vs (ν_{PO}); 1075 vs (ν_{CO}); 945 s (ν_{PO}); 840 s (ν_{POC}); 730 m, 675 m (ν_{aryl}). The ^{31}P NMR spectrum of "$[NP(OCH_2CF_3)_{1.34}(n\text{-}C_4H_9)_{0.33}(C_6H_5)_{0.33}]_n$" contained broad resonances at +39.9 (25), +21.8 (7.5), +11.4 (7.5), and −10.5 (61%) ppm, while the infrared spectrum showed the following peaks (cm^{-1}): 2970 w (ν_{CH}); 1420 m (ν_{POC}); 1280 vs, 1240 s (ν_{PN}); 1160 vs (ν_{PO}); 1070 vs (ν_{CO}); 945 s (ν_{PO}); 845 w (ν_{POC}); 740 vw, 685 vw (ν_{aryl}).

Copolymerization of 5 with $(NPCl_2)_3$. Compounds **5a** (1.31 g, 3.36 mmol) and $(NPCl_2)_3$ (1.26 g, 3.62 mmol) were heated together at 250 °C for 13.5 h. Compound **5b** (2.04 g, 4.70 mmol) and $(NPCl_2)_3$ (1.61 g, 4.63 mmol) were heated together at 250 °C for 5.5 h. The ^{31}P NMR spectrum of the copolymer derived from **5b** and $(NPCl_2)_3$ showed resonances at −1.5 (7), −19.8 (87), and −48.5 (6%) ppm. The polymeric products were derivatized with sodium trifluoroethoxide and were isolated by precipitation techniques as described above. The copolymers (**13**) (from **5a**: 0.93 g, 34%; from **5b**: 1.30 g, 38%) were white, film-forming elastomers. Characterization data are listed in Tables I and IV. The ratio of substituents were determined by ^{31}P NMR spectroscopy and was confirmed by elemental analysis. The infrared spectra of the copolymers were almost identical and showed the following peaks (cm^{-1}): 2950 m, 2880 w (ν_{CH}); 1410 m (ν_{POC}); 1275 vs, 1240 s (ν_{PN}); 1165 vs (ν_{PO}); 1075 vs (ν_{CO}); 955 s (ν_{PO}); 865 m (ν_{POC}); 740 m, 685 m (ν_{aryl}).

Copolymerization of 5a and $N_3P_3Cl_5Me$. Compounds **5a** (1.77 g, 4.55 mmol) and $N_3P_3Cl_5Me$ (1.49 g, 4.55 mmol) were heated together at 250 °C for 29.5 h. The copolymer was treated with sodium trifluoroethoxide and was isolated by precipitation techniques, as described above. The copolymer **16** was found to be a white, film-forming, slightly adhesive elastomer. Characterization data are listed in Tables I and IV. The infrared spectrum of $[NP(OCH_2CF_3)_{1.68}(CH_3)_{0.20}(C_6H_5)_{0.12}]_n$ (**16**) contained the following peaks (cm^{-1}): 2960 m, 2890 w (ν_{CH}); 1410 m (ν_{POC}); 1275 vs, 1230 vs (ν_{PN}); 1165 vs (ν_{PO}); 1080 vs (ν_{CO}); 955 s (ν_{PO}); 865 m (ν_{POC}); 745 w, 685 w (ν_{aryl}). The ratio of substituents was determined by ^{31}P NMR spectroscopy and was confirmed by elemental analysis.

Copolymerization of 6 with $(NPCl_2)_3$. Compound **6a** (1.34 g, 3.64 mmol) was heated with $(NPCl_2)_3$ (1.26 g, 3.62 mmol) at 250 °C during 48.5 h. The reaction between **6b** (1.48 g, 3.60 mmol) and $(NPCl_2)_3$ (1.25 g, 3.60 mmol) required 39.5 h at 250 °C. The contents of each polymerization tube were discolored and nearly immobile. These products were treated with sodium trifluoroethoxide and were purified by reprecipitation techniques, as described above. The copolymer derived from **6a** and $(NPCl_2)_3$ was found to have a molecular weight distribution of 2.1×10^5–$>2 \times 10^6$ by GPC, with a median polymer molecular weight of 1 ×

Table IV
Polymer Analytical and Characterization Data

		elemental anal.					
polymer structure	cyclotriphosphazene precursor	found		calcd		av mol wt (GPC)	T_g, °C
$-[N=P(OCH_2CF_3)_{1.67}(C_6H_5)_{0.33}]_n-$ (**8**)	**5a**	C	27.21	C	27.10	$>1 \times 10^6$	–46.5
		H	2.13	H	2.13		
		N	6.20	N	5.94		
		P	12.95	P	13.14		
$-[N=P(OC_6H_5)_{1.67}(C_6H_5)_{0.33}]_n-$ (**9**)	**5a**	C	62.28[a]	C	63.80	$>1 \times 10^6$	+12.2
		H	4.32[a]	H	4.46		
		N	6.17	N	6.20		
		P	13.57	P	13.71		
$-[N=P(NC_5H_{10})_{1.67}(C_6H_5)_{0.33}]_n-$ (**10**)[b]	**5a**	C	55.89[a]	C	58.82	$>1 \times 10^6$[c]	+75.0
		H	8.22[a]	H	8.77		
		N	16.38[a]	N	17.73		
		P	12.01	P	14.68		
		Cl	1.29[b]	Cl	0		
$-[N=P(OCH_2CF_3)_{1.67}(C_6H_5)_{0.33}]_n-$ (**8**)	**5b**	C	26.97	C	27.10	$>1 \times 10^6$	–48.1
		H	2.20	H	2.13		
		N	5.86	N	5.94		
$-[N=P(OCH_2CF_3)_{1.83}(C_6H_5)_{0.17}]_n-$ (**13**)	**5a** and $(NPCl_2)_3$ (ca. 1:1)	C	24.15	C	23.49	1×10^6	–50.1
		H	1.97	H	1.90		
		N	5.94	N	5.85		
$-[N=P(OCH_2CF_3)_{1.80}(C_6H_5)_{0.20}]_n-$ (**13**)	**5b** and $(NPCl_2)_3$ (ca. 1:1)	C	24.30	C	24.16	1×10^6	–50.6
		H	2.10	H	1.94		
		N	5.90	N	5.87		
$-[N=P(OCH_2CF_3)_{1.68}(CH_3)_{0.20}(C_6H_5)_{0.12}]_n-$ (**16**)	**5a** and $N_3P_3Cl_5Me$ (ca. 1:1)	C	23.34	C	22.99	1×10^6	–49.4
		H	2.24	H	2.06		
		N	6.57	N	6.26		
"$-[N=P(OCH_2CF_3)_{1.34}(C_6H_5)_{0.33}(C_6H_5)_{0.33}]_n-$"	**6a**	C	28.78	C	28.80	3×10^5[d]	
		H	2.55	H	2.58		
		N	6.90	N	6.73		
"$-[N=P(OCH_2CF_3)_{1.34}(C_6H_5)_{0.33}(n\text{-}C_4H_9)_{0.33}]_n-$"	**6b**	C	33.69	C	32.36	3×10^5[e]	
		H	3.46	H	3.32		
		N	6.85	N	6.30		

[a] Average values from several analyses. [b] The removal of HCl is not readily accomplished with piperidino-substituted polymers because of the enhanced basicity of the skeletal nitrogen atoms. Resonances were observed in the ^{31}P NMR spectrum of this polymer at –21 ppm that were attributed to phosphorus environments that were adjacent to nitrogen atoms that had coordinated HCl. [c] This polymer could not be detected by GPC with the use of a differential refractometer; therefore, the molecular weight was estimated by comparison with the trifluoroethoxy- and phenoxy-substituted derivatives. [d] The molecular weight distribution for this polymer was extremely broad. Polymer was detected from 6.5×10^4 to $>2 \times 10^6$, with maxima at 2.5×10^5 and $>2 \times 10^6$. [e] The molecular weight distribution for this polymer was also very broad. Polymer was detected from 3×10^4 to $>2 \times 10^6$, with maxima at 7.5×10^4 and $>2 \times 10^6$.

10^6 and maxima at 3.6×10^5 and $>2 \times 10^6$. The ^{31}P NMR spectrum contained a resonance at –9.4 ppm (83%) that was consistent with the presence of $P(OCH_2CF_3)_2$ groups, and several broad resonances at 30–40 ppm (17%). The copolymer derived from **6b** and $(NPCl_2)_3$ was found to have a molecular weight distribution of 3.3×10^5–$>2 \times 10^6$, with a median molecular weight of 1×10^6 and maxima at 5.4×10^5 and $>2 \times 10^6$. The ^{31}P NMR spectrum contained a resonance at –9.7 (69%, $P(OCH_2CF_3)_2$) and several resonances at 36–42 ppm.

Polymerization of $N_3P_3Cl_4BrMe$. The compound $N_3P_3Cl_4BrMe$ (3.46 g, 9.31 mmol) was heated at 250 °C for 1.5 h. After this time, the contents of the tube were virtually immobile and slightly yellow. A typical conversion to polymer was 77–88%. The halogeno polymer was analyzed by ^{31}P NMR spectroscopy (Table II) and was derivatized with sodium trifluoroethoxide and isolated by precipitation, as described earlier. The polymer was recovered (2.1 g, 48%) as a white, elastomeric material. It was identical with that reported previously prepared from $N_3P_3Cl_5Me$.[17] The molecular weight of the polymer was found to be $>1 \times 10^6$ by GPC. The infrared spectrum showed the following peaks (cm^{-1}): 2970 m, 2900 w (ν_{CH}); 1420 m (ν_{POC}); 1280 vs, 1235 s (ν_{PN}); 1170 vs (ν_{PO}); 1070 vs (ν_{CO}); 945 s (ν_{PO}); 855 m (ν_{POC}); 640 w (CF_3). The ^{31}P NMR spectrum contained resonances at +18.7 (35%, $P(Me)(OCH_2CF_3)$) and –8.1 (65%, $P(OCH_2CF_3)_2$) ppm.

Polymerization of $(NPBr_2)_3$. Hexabromocyclotriphosphazene, $(NPBr_2)_3$ (2.65 g, 4.31 mmol), was heated at 220 °C for 6.5 h, after which time the molten reaction mixture was light brown in color and almost immobile. The polymeric material was removed from the tube and was washed with several portions of hot toluene to remove cyclic species. The material was found to be insoluble in 1,4-dioxane, toluene, or benzene. (THF could not be used because the P–Br bonds may react with this solvent.) However, because the material swelled sufficiently in toluene, a ^{31}P NMR spectrum could be obtained (Table II).

Copolymerization of $(NPBr_2)_3$ and $(NPCl_2)_3$. Species $(NPBr_2)_3$ (1.0 g, 1.63 mmol) and $(NPCl_2)_3$ (0.57 g, 1.63 mmol) were heated together in a sealed tube at 220 °C for 18–24 h, or at 200 °C for 82.5 h. In all cases, the contents of the polymerization tubes discolored and immobilization occurred rapidly. The copolymer was removed from the tube and was washed with several portions of hot toluene to remove any cyclophosphazenes. The copolymers were insoluble in 1,4-dioxane, toluene, or benzene. However, the materials swelled sufficiently in toluene to allow a ^{31}P NMR spectrum to be obtained (Table II).

Analysis of Halogen-Substituted Cyclic and Polymeric Phosphazenes by ^{31}P NMR Spectroscopy. The halogenophosphazene polymers, copolymers, and cyclic products derived from heating **5**, **6**, $N_3P_3Cl_5Me$, $N_3P_3Cl_4BrMe$, $(NPCl_2)_3$, or $(NPBr_2)_3$ in sealed tubes were analyzed by ^{31}P NMR spectroscopy. The products were analyzed by opening the polymerization tubes in a nitrogen-filled glovebag, followed by transfer of the contents to a Schlenk flask and addition of a minimum quantity of toluene. Aliquots of the reaction products were withdrawn via syringe under a blanket of nitrogen and were introduced into an NMR tube that was prefilled with nitrogen. For specific cases, as described below, the polymers were separated from the cyclic species by precipitation into a nonsolvent, and the products were analyzed separately.

Heating of 5b at Temperatures Insufficient to Promote Polymerization. A sample of **5b** (1.96 g, 4.52 mmol) was heated at 178 °C for 72 h. Under these conditions, no polymerization was detected (by ^{31}P NMR spectroscopy). The cyclic products consisted of **5a** (12%), 18 (3%), and unreacted **5b** (85%), as deduced by ^{31}P NMR spectroscopy. An analysis of the cyclic species by gas chromatography indicated that the proportions were

5a (17%), **5b** (80%), and **18** (3%).

A sample of **5b** was heated independently at 182 °C for 72 h. A ^{31}P NMR analysis indicated that approximately 3% of the cyclic species had been converted to polymer. The ^{31}P NMR spectrum of the cyclic products was consistent with a mixture that consisted of unreacted **5b** (53%), **5a** (36.5%), and **18** (10.5%). A GC/MS analysis of the product mixture confirmed the assignments and indicated a product ratio of **5a** (34%), **5b** (56%), and **18** (9%). Compound **5a** was detected first by the parent (plus proton) ion (*m/e* 388) with a Cl_5 isotope pattern. A Cl_4 pattern was also observed (*m/e* 352) for loss of chlorine. Compound **5b** eluted next, and the mass spectrum contained a parent (plus proton) ion (*m/e* 432) with a Cl_4Br isotope pattern. Other peaks were observed that corresponded to loss of chlorine (*m/e* 396, Cl_3Br isotope pattern) and loss of bromine (*m/e* 352, Cl_4 isotope pattern). Compound **18** was identified in the mass spectrum by the presence of a parent (plus proton) ion (*m/e* 476) with a Cl_3Br_2 isotope pattern and by the presence of peaks that corresponded to loss of chlorine (*m/e* 440, Cl_2Br_2 isotope pattern) and to loss of bromine (*m/e* 396, Cl_3Br isotope pattern). A cyclotriphosphazene that was not detected from the ^{31}P NMR spectrum of the reaction products, but was detected by GC/MS, was tentatively identified as **19**. This compound yielded a parent (plus proton) ion (*m/e* 524, calcd *m/e* 520) in the mass spectrum with an unresolved Cl_2Br_3 isotope pattern. An unresolved $ClBr_3$ pattern (*m/e* 486, calcd *m/e* 484) was detected for the loss of chlorine from the parent ion, and a Cl_2Br_2 isotope pattern (*m/e* 440, calcd *m/e* 440) was observed for loss of bromine. The very low concentration of this species ($\simeq$1.0%) in the product mixture was responsible for the poor statistical analysis of the mass-spectral data. Therefore, the isotope patterns for the parent (plus proton) and parent minus chlorine ions were not fully resolved and not all peaks in the isotope pattern were observed. These GC/MS data formed the basis for the identification of the products derived from the polymerization of **5b** at higher temperatures.

Isolation of Polymer 17. A sample of polymer **17** was obtained from the polymerization of **5b** (1.96 g, 4.52 mmol) at 250 °C, as described previously. Resonances were detected in the ^{31}P NMR spectrum of the polymer sample that corresponded to P(Ph)Cl (27%), PCl_2 + P(Ph)Br (58%), PClBr (11%), and PBr_2 (4%).

The crude polymer was precipitated from a minimum of toluene into dry hexanes (250 mL). The adhesive elastomer was redissolved in a minimum volume of toluene. The ^{31}P NMR spectrum of the precipitated polymer was virtually identical with that of the crude polymer, with resonances detected for P(Ph)Cl (26%), PCl_2 + P(Ph)Br (58%), PClBr (13%), and PBr_2 (3%). No cyclic phosphazenes were detected in the ^{31}P NMR spectrum of polymer **17** after the reprecipitation process. A ^{31}P NMR and gas-chromatographic analysis of the cyclic species obtained from the reaction mixture showed the presence of **5a** (49%), **5b** (40%), and **18** (11%). Other similar experiments showed only the presence of **5a**.

Monitoring of the Polymerization of 5b at 250 °C by ^{31}P NMR Spectroscopy. Each of four polymerization tubes was charged with pure **5b** (ca. 1.5 g). The tubes were heated at 250 °C and were withdrawn after 2, 4, 6, and 9 h, respectively. The reaction products were dissolved in a minimum volume of toluene and were analyzed by ^{31}P NMR spectroscopy. The results are listed in Table III. After 2-h reaction, an analysis of the ^{31}P NMR spectrum and gas-chromatographic profile indicated that the cyclic products consisted of **5a** (19%), **5b** (77%), and **18** (4%). The ^{31}P NMR spectrum was compatible with a cyclic mixture of ca. 33% **5a** after 4 h, and 62% **5a** after 6 h.

Interaction of $(NPCl_2)_n$ and 5b at 182 °C. A mixture of $(NPCl_2)_n$ (0.61 g, 5.26 mmol) and **5b** (1.49 g, 3.44 mmol), purified as described previously, was heated in a polymerization tube at 182 °C for 72 h. The tube was then allowed to cool to room temperature, and the polymer was recovered by precipitation from toluene into dry hexane. An analysis of the ^{31}P NMR spectrum of the polymer redissolved in toluene indicated the presence of PCl_2 (96%) and PClBr (4%) units. The cyclic products were analyzed by ^{31}P NMR spectroscopy and gas chromatography and were found to consist of **5a** (49%), **5b** (36%), **18** (12%), and **19** (3%).

Interaction of 17 and 5a at 182 °C. Polymer was prepared and isolated by precipitation techniques, as described previously. Resonances were detected in the ^{31}P NMR spectrum of **17** that corresponded to P(Ph)Cl (30%), PCl_2 + P(Ph)Br (53%), PClBr (14%), and PBr_2 (3%). Polymer **17** (0.2 g) and **5a** (0.84 g, 2.16 mmol) were then heated in a polymerization tube at 182 °C for 72 h. The tube was then allowed to cool to room temperature, and the polymer was recovered by precipitation from toluene into dry hexane. A ^{31} NMR spectrum of the redissolved polymer was compatible with a structure that contained P(Ph)Cl (31%), PCl_2 + P(Ph)Br (62%), and PClBr (7%) units. The cyclic species were analyzed by ^{31}P NMR spectroscopy and gas chromatography and were found to contain **5a** (94%), **5b** (6%), and **18** (0.2%).

Polymerization of $(NPCl_2)_3$ in the Presence of 5a, 5b, $N_3P_3Cl_5Me$, $N_3P_3Cl_4BrMe$, or Br_2. Special care was taken to exclude traces of moisture from these polymerization mixtures. The cyclophosphazenes were handled in an inert atmosphere after the final sublimation. Polymerization tubes were connected to a vacuum line (0.05 torr) after the standard drying procedure and were flame dried. The tubes were allowed to cool to room temperature while attached to the vacuum line and then were transferred to an inert atmosphere chamber, charged with the polymerization mixture, and sealed off. Each tube contained $(NPCl_2)_3$ (15.0 ± 0.5 g) (alone for the control) plus 1.0 mol % of the appropriate additive. Duplicate polymerizations were run in each case.

Acknowledgment. We thank the Office of Naval Research for the support of this work. We also thank the National Science Foundation Polymers Program for providing a Perkin-Elmer 283B infrared spectrometer. J. L. Desorcie is acknowledged for recording several of the ^{31}P and ^{1}H NMR spectra, and G. Hancock and R. D. Minard are acknowledged for recording the gas chromatography/mass spectrometry data. We are grateful to R. E. Singler and J. Yeaton of the Army Materials and Mechanics Research Center for obtaining the T_g data.

References and Notes

(1) (a) This work was presented, in part, at the 187th National Meeting of the American Chemical Society, St. Louis, MO, April 8–13, 1984. See: Connolly, M. S.; Allcock, H. R. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1984**, *25*, 162. (b) For a previous paper in this series, see: Allcock, H. R.; Connolly, M. S.; Harris, P. J. *J. Am. Chem. Soc.* **1982**, *104*, 2482.

(2) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.

(3) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.

(4) Allcock, H. R.; Kugel, R. L. *Inorg. Chem.* **1966**, *5*, 1716.

(5) Allcock. H. R.; Cook, W. J.; Mack, D. P. *Inorg. Chem.* **1972**, *11*, 2584.

(6) Allcock, H. R. "Phosphorus–Nitrogen Compounds", Academic Press: New York, 1972.

(7) Tate, D. P. *J. Polym. Sci., Polym. Symp.* **1974**, *48*, 33.

(8) Singler, R. E.; Schneider, N. S.; Hagnauer, G. L. *Polym. Eng. Soc.* **1975**, *15*, 322.

(9) Allen, G.; Mortier, R. M. *Polymer* **1972**, *13*, 253.

(10) Liu, C. F.; Evans, R. L. U.S. Patent 3169933, 1965.

(11) MacCallum, J. R.; Tanner, J. *J. Polym. Sci., Part A-1* **1968**, *6*, 3163.

(12) Allcock, H. R.; Chu, C.-T.-W. *Macromolecules* **1979**, *12*, 551.

(13) (a) Neilson, R. H.; Wisian-Neilson, P. *J. Am. Chem. Soc.* **1980**, *102*, 2848. (b) Neilson, R. H.; Wisian-Neilson, P. *J. Macromol. Sci., Chem.* **1981**, *A16*, 425.

(14) Allcock, H. R.; Moore, G. Y. *Macromolecules* **1975**, *8*, 377.

(15) Allcock, H. R.; Harris, P. J.; Connolly, M. S. *Inorg. Chem.* **1981**, *20*, 11.

(16) Allcock, H. R.; Harris, P. J. *Inorg. Chem.* **1981**, *20*, 2844.

(17) Allcock, H. R.; Ritchie, R. J.; Harris, P. J. *Macromolecules* **1981**, *13*, 1332.

(18) Allcock, H. R.; Connolly, M. S.; Whittle, R. R. *Organometallics* **1983**, *2*, 1514.

(19) When **6a** was heated at 178 °C for 72 h, no degradation or polymerization was observed, as determined by ^{31}P NMR spectroscopy and gas chromatography. Therefore, degradation must occur at higher (250 °C) temperatures and could accompany the polymerization.

(20) The peak integration areas for each type of phosphorus atom varied with the reaction conditions. For polymer **17**, the areas were in the range –1.5 (9–30), –19.8 (53–84), –48.5 (5–20), and –79.6 (2–4%) ppm. For the polymer derived from $N_3P_3Cl_4BrMe$, the areas were in the range of +10.3 (8–30), –8.1

1340 *Macromolecules* **1985**, *18*, 1340-1345

(9-31), -20.4 (44-59), -48.9 (3-12), and -79.6 (0-5%) ppm. The areas were in the range -19.5 (20-26), -47.5 (33-44), and 79.3 (36-41%) ppm for the copolymer derived from $(NPCl_2)_3$ and $(NPBr_2)_3$.

(21) Allcock, H. R.; Gardner, J. E.; Smeltz, K. M. *Macromolecules* **1975**, *8*, 36.

(22) Allcock, H. R.; Best, R. J. *Can. J. Chem.* **1964**, *42*, 447.

(23) As discussed previously, the conversion of $N_3P_3Cl_4BrMe$ to its high polymer is also accompanied by halogen migration from one repeating unit to another. New cyclic, trimeric phosphazenes were also formed by halogen scrambling processes and were identified by ^{31}P NMR spectroscopy, gas chromatography, and mass-spectrometric techniques (chemical ionization). In a typical experiment, $N_3P_3Cl_5Me$ (32%, P + 1 at *m/e* 326), *gem*-Me-Br-$N_3P_3Cl_4$ (34%, P + 1 at *m/e* 370), *non-gem*-Me-Br-$N_3P_3Cl_4$ (4%, P + 1 at *m/e* 370), *non-gem*-$N_3P_3Cl_3Br_2Me$ (22%, P + 1 at *m/e* 414), and $N_3P_3Cl_2Br_3Me$ (7%, P + 1 at *m/e* 458) were identified as cyclic products. The latter two products are methyl-substituted analogues of **18** and **19**, **20**. The formation of *non-gem*-Me-Br-$N_3P_3Cl_4$ was unexpected, and was not observed for the phenyl analogue.

(24) Because the conversion to polymer was so high (see Experimental Section), typically only 100-200 mg of cyclic phosphazenes were recovered. While ^{31}P NMR spectroscopy was useful to identify qualitatively the presence of P(Ph)Cl, PCl_2, and PClBr resonances, gas chromatography was a more accurate method to determine the relative proportions of **5a**, **5b**, **18**, and **19** in the product mixtures. Unless noted otherwise, the product ratios were from gas-chromatographic analyses.

(25) At this stage in the reaction, the ratio of cyclic species was very similar to that obtained by heating **5b** at 178 °C for 72 h.

(26) The small amount of scrambling and low yield of polymer after 2 h was not surprising, as studies with melting point standards indicated that 1.5 h was required, on the average, for the contents of the polymer tubes to reach 250 °C.

(27) Jordan, A. D.; Cavell, R. G. *Inorg. Chem.* **1972**, *11*, 564.

(28) Groenweghe, L. C. D.; Payne, J. H., Jr. *J. Am. Chem. Soc.* **1959**, *81*, 6357.

(29) Fluck, E.; Van Wazer, J. R.; Groenweghe, L. C. D. *J. Am. Chem. Soc.* **1959**, *81*, 6363.

(30) Schwarzmann, E.; Van Wazer, J. R. *J. Am. Chem. Soc.* **1959**, *81*, 6366.

(31) Failure to dry the bromine adequately results in a polymerization rate *increase*, but this effect can be attributed to the catalytic influence of water.[21]

(32) Polymerization of $(NPCl_2)_3$ in the presence of Br_2 brought about a curious change in the physical properties of the $(NPCl_2)_n$ high polymer, changes that could be attributed to a decrease in crystallinity. However, after treatment of the $(NPCl_2)_n$ with sodium trifluoroethoxide, the resultant $[NP(OCH_2CF_3)_2]_n$ was identical in molecular weight and appearance with that derived from pure $(NPCl_2)_3$. The lower yield of the resultant $[NP(OCH_2CF_3)_2]_n$, relative to the control, could indicate that a significant amount of lower molecular weight species was also formed.

(33) Pauling, L. "The Nature of the Chemical Bond"; Cornell University Press: Ithaca, NY, 1960.

(34) Kauffman, G. B.; Teter, L. A. *Inorg. Synth.* **1963**, *7*, 9.

Ring-Opening Polymerization of Metallocene Cyclophosphazene Derivatives

Harry R. Allcock,* Karen D. Lavin, and Geoffrey H. Riding

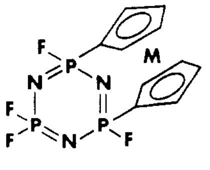
Department of Chemistry, The Pennsylvania State University, University Park, Pennsylvania 16802. *Received June 14, 1984*

ABSTRACT: New and unusual metallocenylphosphazene high polymers have been prepared by the thermal ring-opening polymerization of metallocene-substituted cyclotriphosphazene derivatives. The transannular-linked cyclic trimers $[N_3P_3F_4(\eta\text{-}C_5H_4)_2M]$ (**1a**, M = Fe; **1b**, M = Ru) and the monosubstituted compounds $[N_3P_3F_5(\eta\text{-}C_5H_4)M(\eta\text{-}C_5H_5)]$ (**2a**, **2b**) serve both as reaction model compounds and as "monomers" for the analogous high polymeric derivatives **3a**, **3b**, and **8a**, **8b**. The hydrolytically unstable P-F bonds in the trimers and high polymers were replaced by treatment with sodium trifluoroethoxide to yield the corresponding air-stable trimeric and polymeric metallocenyl(trifluoroethoxy)phosphazenes (**4a**, **4b**, **9a**, **9b**). Compounds **1a** and **1b** were also copolymerized to yield a 1:1 copolymer which, after reaction with sodium trifluoroethoxide, yielded $[N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Fe\text{-}N_3P_3(OCH_2CF_3)_4(\eta\text{-}C_5H_4)_2Ru]_n$ (**7**). The properties, structure, and characterization of these new organometallic polyphosphazenes are discussed, together with the mechanism of thermal polymerization of cyclic phosphazenes.

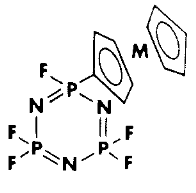
Introduction

The study of the iron group metallocenes has been one of the most active areas of chemistry since the discovery of ferrocene in 1951.[1] At the present time, considerable interest exists in the synthesis of metallocenes that are linked to macromolecules. Such polymers are important as prospective catalyst systems, electrode mediators, or electroactive solid-state materials.

In recent months, we have reported a number of different methods for the linkage of organometallic units to small molecule phosphazene rings.[2-9] These reactions have been developed as prototypes for the corresponding reactions of linear phosphazene high polymers. As part of that program, we reported recently the synthesis of the first cyclophosphazenes that bear metallocene side groups.[10,11] Two of these species are shown in structures **1** and **2**.



1a,b



2a,b

a, M=Fe; b, M=Ru

The availability of species **1** and **2** provides two potential routes for the synthesis of the corresponding linear high polymers. First, the high polymeric analogues of **1** and **2** might be prepared by the reactions of poly(difluorophosphazene), $(NPF_2)_n$, with mono- or dilithiometallocenes. This possibility is under investigation in our laboratory. Alternatively, **1** and **2** might be used as "monomers" for direct phosphazene ring-opening polymerization to the corresponding linear high polymers. Such a reaction would be analogous to the known polymerization

0024-9297/85/2218-1340$01.50/0