Poly(monophosphazophosphazenes): New Polymers with N=PR$_3$ Side Groups

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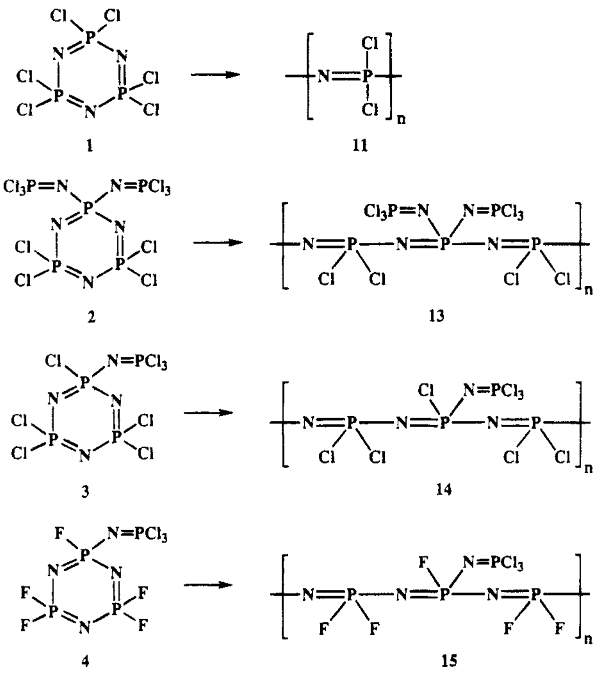
ABSTRACT: Phosphazene high polymers with N=PR$_3$ (phosphazo) side groups are of interest from both the theoretical and potential technological points of view. High polymeric monophosphazophosphazenes were prepared with trifluoroethoxy, phenoxy, anilino, and propylamino side groups. Small-molecule cyclic counterparts were also synthesized as model systems for the macromolecular reactions. These compounds were prepared using both (trichlorophosphazo)pentachlorocyclotriphosphazene (N$_3$P$_3$Cl$_5$NPCl$_3$) and (trichlorophosphazo)pentafluorocyclotriphosphazene (N$_3$P$_3$F$_5$NPCl$_3$) as the starting materials. Specifically, the synthesis of monophosphazophosphazene polymers through the thermal ring-opening polymerization of N$_3$P$_3$Cl$_5$NPCl$_3$ at 150-180 °C or of N$_3$P$_3$F$_5$NPCl$_3$ at 200-210 °C is reported. Differences in the reactivity of the phosphazochloro- and the phosphazofluorophosphazenes to halogen replacement reactions were found at both the cyclic trimeric and high polymeric levels. In general, replacement of the chlorine atoms by organic groups was achieved with greater ease than the replacement of fluorine atoms. For the reagents studied, the replacement of halogen atoms by sodium trifluoroethoxide was more facile than with the other nucleophiles. A comparison is made between the properties of monophosphazophosphazenes, classical phosphazenes, and 1,1-diphosphazophosphazenes.

Introduction

Most polyphosphazenes are prepared by the thermal ring-opening polymerization of hexachlorocyclotriphosphazene (**1**) followed by replacement of the chlorine atoms in the polymer by a wide variety of organic nucleophiles.[1-4] This approach has provided a large number of polymers in which the physical and chemical properties are determined mainly by the characteristics of the side groups. A knowledge of the structure-property relationships in these systems provides the potential for macromolecular and materials design.

Many opportunities exist for the design and synthesis of polymers that contain a phosphazene backbone but with inorganic units forming part of the side group structure. These largely inorganic polymers have a variety of potential applications, particularly in the field of fire-retardant materials.[5] We are investigating the ring-opening polymerization of several cyclic phosphazene "monomers" that lead to such polymers.[6,7] These include phosphazocyclotriphosphazenes, which are species that bear a short phosphorus-nitrogen-based side unit linked to the main skeletal system. Fundamental interest in the synthesis and reactions of small-molecule phosphazophosphazenes has been evident for 30 years,[8-17] but until recently that interest was not translated into macromolecular chemistry. In a recent paper, we reported the first polymerization of a cyclic phosphazene that bears two phosphazo units linked geminally to the ring, specifically 1,1-bis(trichlorophosphazo)tetrachlorocyclotriphosphazene (**2**) (Scheme 1). In our earlier work, we found that trimer **2** polymerized at 150 °C. It was subsequently shown that the replacement of the chlorine atoms in the polymer by aryloxy or alkoxy nucleophiles can be accomplished to give hydrolytically stable organoderivatives.[18] Studies of phosphazophosphazenes allow the influence of the N-P side groups on the properties of the polymer to be evaluated together with their function as short, branched units.

Scheme 1



In this paper, we report the syntheses of both small-molecule cyclic trimeric and linear high polymeric monophosphazophosphazenes utilizing two starting cyclic trimers, (trichlorophosphazo)pentachlorocyclotriphosphazene (**3**) and (trichlorophosphazo)pentafluorocyclotriphosphazene (**4**), as "monomers" (see Scheme 1). The resultant linear high polymers with their short-chain phosphazene branch units were treated with sodium trifluoroethoxide, sodium phenoxide, *n*-propylamine, or aniline to yield stable poly[(organophosphazo)phosphazenes]. The presence of the side group phosphazo units may be important for tailoring the properties of the polymer by the selective introduction of different side groups at the main chain and phosphazo

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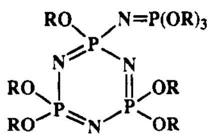
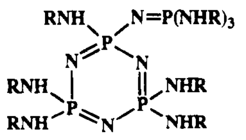
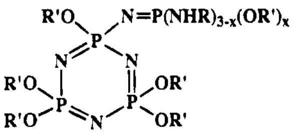
Chart 1



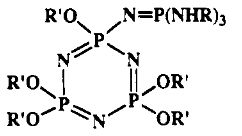
5 OR= OCH_2CF_3
6 OR= OC_6H_5



7 HNR= HNC_6H_5
9 HNR= $HNCH_2CH_2CH_3$



8 NHR= NHC_6H_5
OR'= OCH_2CF_3, x= 0-2



10 HNR= $HNCH_2CH_2CH_3$
OR'= OCH_2CF_3

sites. One of the reasons for our interest in poly(monophosphazophosphazenes) is that they may yield polymers with properties that are intermediate between those of the classical polyphosphazenes and poly(diphosphazophosphazenes).

The main objectives of this study were (1) to determine the conditions necessary for the thermal ring-opening polymerization of the monophosphazo cyclic trimers, (2) to examine the reactivities of the resultant high polymers to alkoxy, aryloxy, and amino nucleophiles, and (3) to compare the properties of the new polymers with those of poly(1,1-diphosphazophosphazenes) and classical polyphosphazenes. The structures of the newly synthesized polymers and trimers, as well as the structures of related, previously described compounds, are shown in Scheme 1, Chart 1, and Chart 2.

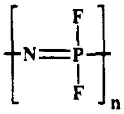
Results and Discussion

Polymerization of 3 and 4 and Characterization of Polymers 14 and 15. Hexachlorocyclotriphosphazene (**1**) undergoes thermal ring-opening polymerization at 250 °C. As stated earlier, we found previously that the diphosphazo trimer (**2**) undergoes thermal ring-opening polymerization at only 150 °C. This provided a starting point for finding the conditions needed for polymerization of the monophosphazo trimers.

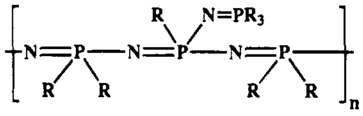
Polymers **14** and **15** were formed by the thermal ring-opening polymerization of cyclic trimers **3** and **4**, at 150–180 and 200–210 °C, respectively. The unreacted trimers were removed from the polymers by extraction with warm heptane. Both halogeno polymers are moisture-sensitive at this stage and must be manipulated under an atmosphere of dry argon.

The polymerizations were accompanied by an increase in the melt viscosity of the system and by changes in the ^{31}P nuclear magnetic resonance (NMR) shifts that were compatible with the formation of linear or macrocyclic polymers (see Figures 1 and 2). The NMR peaks for polymer **14** were sharp, which suggested a regular head-to-tail microstructure: a more complex microstructure would be expected to give rise to a more complicated NMR spectrum or to peak broadening. A similar microstructure was inferred for polymer **15**. This is supported by analysis of the products formed by the reactions of **14** and **15** with sodium trifluoroethoxide. The products formed from both reactions were the same, which strongly suggested that **14** and **15** had similar microstructures (see reactivity section). Polymer **15** is soluble in nonfluorinated solvents such as toluene and methylene chloride. This provides an important difference from poly(difluorophosphazene) (**12**), which is soluble only in perfluorinated solvents. Thus, polymer **15** offers more opportunities for reaction chemistry than does **12**.

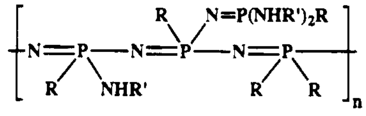
Chart 2



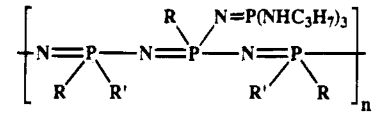
12



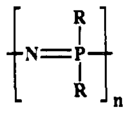
16 R= OCH_2CF_3
17 R= OC_6H_5
18 R= NHC_6H_5
20 R= $NHCH_2CH_2CH_3$



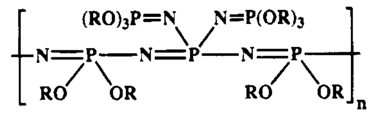
19 R= OCH_2CF_3, R'= C_6H_5
Idealized structure



21 R= OCH_2CF_3, R'= NHC_3H_7
Idealized structure



22 R= OCH_2CF_3
23 R= OC_6H_5
24 R= NHC_6H_5
25 R= NHC_3H_7



26 R= CH_2CF_3
27 R= C_6H_5

Proposed Polymerization Mechanism. The accepted mechanism for the thermal ring-opening polymerization of cyclophosphazenes involves an ionization of phosphorus–halogen bonds. The subsequent attack on this phosphorus cation by a nitrogen lone pair from a separate phosphazene trimer and opening of the phosphazene ring lead eventually, by a cationic propagation process, to formation of the high polymer. However, cyclophosphazenes with strained rings may undergo thermal ring-opening polymerization even in the absence of an easily ionizable phosphorus–halogen side unit.[19] Thus, the polymerization of cyclophosphazene compounds can be understood in terms of both ring strain and ionization.

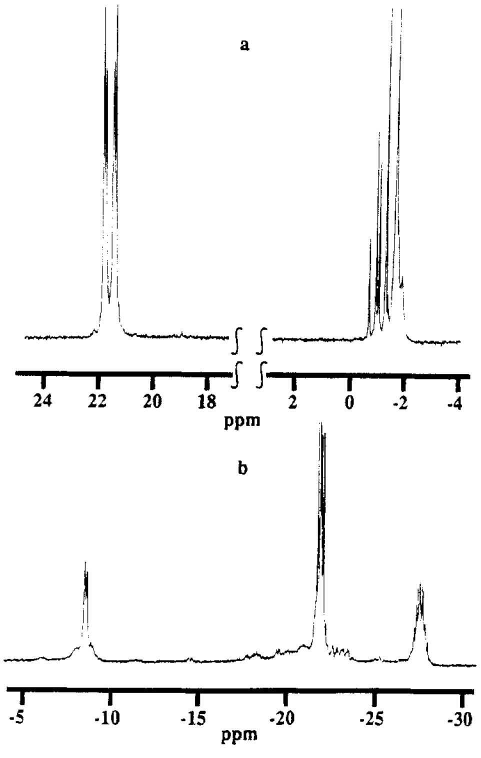


Figure 1. ^{31}P NMR spectra of (a) trimer **3** in $CDCl_3$ and (b) polymer **14** in $CDCl_3$.

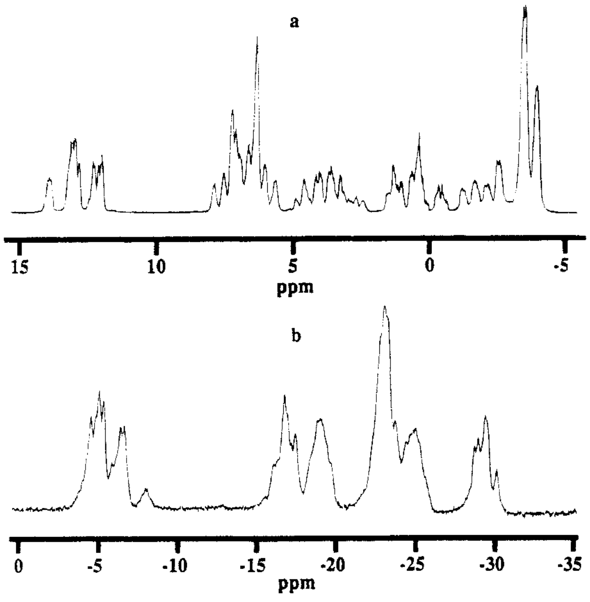
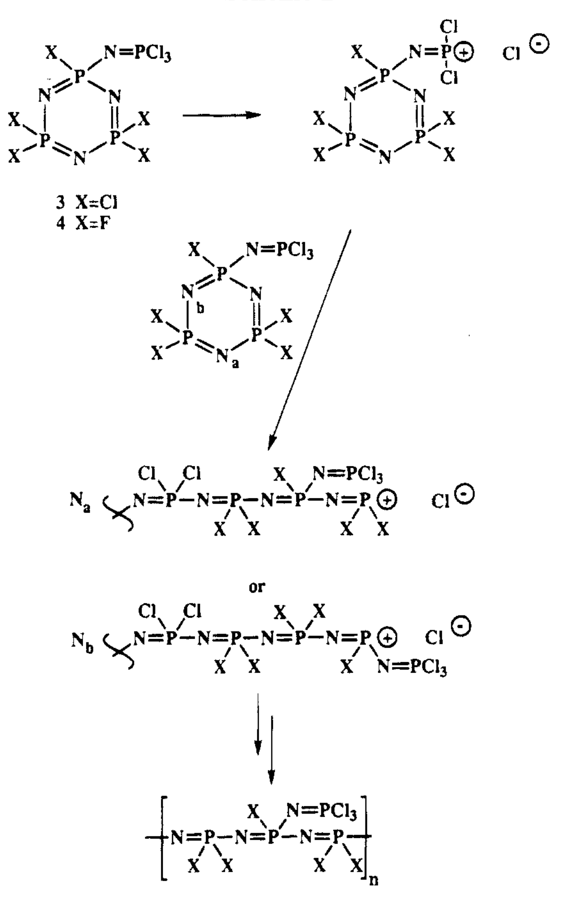


Figure 2. ^{31}P NMR spectra of (a) trimer **4** in $CDCl_3$ and (b) polymer **15** in $CDCl_3$.

The polymerization of phosphazophosphazenes provides additional information about the ring-opening polymerization of phosphazenes. The temperatures required for polymerization of trimers **3** and **4** are intermediate between the temperatures required for polymerization of **1** (250 °C) and **2** (150 °C). The polymerizations discussed here can be understood in terms of an ionization mechanism similar to the one proposed for 1,1-diphosphazophosphazenes.[18] Ionization of a phosphorus–chlorine bond yields an initiating species (see Scheme 2). Each phosphazo side unit bears a $-PCl_3$ terminal unit, which is believed to be more reactive to heterolytic P–Cl cleavage than the ring $P-Cl_2$ units.[18,20] This is supported by two pieces of evidence. First, when nucleophiles such as sodium phenoxide were added to the trimers, substitution occurred first by replacement of the exocyclic chlorine atoms. Second, trimer **3** appeared to initiate the ring-opening polymerization of tetrahydrofuran (THF). For example, the ^{13}C NMR spectrum of THF changed after several days in the presence of **3** at room temperature in a manner consistent with the formation of poly(tetramethylene oxide). The solution viscosity also increased during this process. THF is known to undergo cationic-initiated polymerization, which suggests that a cationic species was present in solution. The same behavior was found for **2**[18] but not for **1**. The exocyclic chlorine atoms presumably ionize more easily and allow lower polymerization temperatures compared to hexachlorocyclotriphosphazene. Trimer **4** appeared unable to initiate the polymerization of THF under similar conditions. After 3 weeks at room temperature, the ^{13}C NMR spectrum showed no evidence for the presence of poly(tetramethylene oxide). Trimer **4** required a higher temperature for self-polymerization than did trimer **3**, presumably because it bears the more electronegative fluorine atoms on the ring. This could limit the ionization of a P–Cl bond. The role of ring strain in trimers **3** and **4** is more difficult to assess. Past work has shown that ionization without polymerization is possible.[21] Therefore, inherent ring strain, similar to that suggested by molecular modeling of **2**,[18] may play a part in the ring-opening polymerization.

Scheme 2



Reactivity Studies. Initially, the substitution reactions were investigated at the small-molecule cyclic trimeric level. These reactions were used as models for the analogous macromolecular substitution reactions. The four nucleophiles selected were chosen because they covered a range of nucleophilicity and steric bulk. The cyclic trimeric products were characterized by ^1H NMR, ^{31}P NMR, ^{13}C NMR, elemental analysis, and mass spectrometry (see Table 1).

Table 1. Cyclic Trimer Characterization Data[a]

compd	^{31}P NMR	^{1}H NMR	^{13}C NMR	elem. anal.
5	P_b −7.9 (d, $J_{P_bP_c}$ = 76. Hz) P_c 7.5 (dt) P_a 17.3 (d, $J_{P_aP_c}$ = 87 Hz)	4.1 (m, 2H) 4.3 (m, 8H) 4.5 (m, 6H)	61.9 (q, $^2J_{CF}$ = 37 Hz) 62.7 (q, $^2J_{CF}$ = 37 Hz) 64.9 (q, $^2J_{CF}$ = 38 Hz) 65.0 (q, $^2J_{CF}$ = 38 Hz) 121.7 (q, J_{CF} = 277 Hz) 121.8 (q, J_{CF} = 277 Hz) 122.4 (q, J_{CF} = 277 Hz)	calcd C, 19.77; H, 1.66; N, 5.76 found C, 19.32; H, 1.55; N, 5.76
6	P_b −25.4 (d, $J_{P_bP_c}$ = 73 Hz) P_c 2.2 (dt) P_a 9.1 (d, $J_{P_aP_c}$ = 82 Hz)	7.1 (m)	120.5, 120.6, 121.0, 121.2, 121.5, 121.6, 124.2, 124.3, 125.7, 128.8, 129.2, 129.8	calcd C, 62.32; H, 4.36; N, 6.06 found C, 62.54; H, 4.56; N, 6.05
7	P_b −12.1 (d, $J_{P_bP_c}$ = 58 Hz) P_c −1.0 (dt) P_a −4.2 (d, $J_{P_aP_c}$ = 73 Hz)	7.1 (m) 6.8 (m)	118.5, 118.6, 119.4, 120.6, 121.0, 129.2, 129.4, 129.7, 141.5, 142.5, 113.1, 117.2, 124.9	calcd C, 62.86; H, 5.06; N, 18.33; Cl, 0.00 found C, 60.17; H, 5.70; N, 17.40; Cl, 0.31
9·HCl	P_c −2.4 (m) P_b 13.7 (d) P_a 14.9 (br s)	0.9 (m, 3H, CH_3) 1.6 (m, 2H, CH_2CH$_3$) 2.9 (m, 2H, NHCH_2) 3.6 (br s, 1H, NH)	11.5 (CH$_3$) 24.9 (CH$_2$CH$_3$) 42.8 (NHCH$_2$)	calcd C, 42.29; H, 9.62; N, 24.67; Cl, 5.21 found C, 42.10; H, 9.84; N, 24.66; Cl, 5.48
10	P_c 8.2 (dt) P_b 14.0 (d, $J_{P_bP_c}$ = 52 Hz) P_a 17.9 (d, $J_{P_aP_c}$ = 72 Hz)	0.9 (m, 9H, CH_3) 1.5 (m, 6H, CH_2CH$_3$) 2.7 (m, 3H, NH) 2.8 (m, 6H, NHCH_2) 4.1 (m, 2H, CH_2CF$_3$) 4.25 (m, 8H, CH_2CF$_3$)	11.0 (CH$_3$) 24.7 (CH$_2$CH$_3$) 42.7 (NHCH$_2$) 62.1 (m, CH$_2$CF$_3$) 123.9 (q, J_{CF} = 277, CF$_3$) 123.8 (q, J_{CF} = 277, CF$_3$) 122.8 (q, J_{CF} = 277, CF$_3$)	calcd C, 26.86; H, 4.03; N, 11.55 found C, 27.28; H, 4.17; N, 11.47

[a] $P_a \equiv PR_2$, $P_b \equiv PR$, $P_c \equiv PR_3$.

(1) Small-Molecule Substitution Reactions. (a) Sodium Trifluoroethoxide as a Nucleophile. The reaction of **3** or **4** with sodium trifluoroethoxide proceeded readily to give the fully substituted trimer **5**. Products obtained from either trimer **3** or **4** yielded the same characterization data for trimer **5**.

(b) Sodium Phenoxide as a Nucleophile. The reaction of **3** with sodium phenoxide at reflux in dioxane for 72 h resulted in complete replacement of the halogen atoms to give compound **6**. By contrast, the reaction of the fluoro/chloro species, **4**, carried out for 1 week at reflux in dioxane gave a mixture of phenoxy–substituted trimers with one or two unreacted fluorine atoms. In agreement with work published earlier,[22] the unreacted P–F bond in the monofluoro product is geminal to the phosphazo unit. This difference in reactivity may reflect an $S_N1(P)$ type mechanism available to the chloro derivative **3**. The fluoro derivative, **4**, required more forcing conditions due to a presumed $S_N2(P)$ mechanism throughout the process.[22,23]

(c) Aniline as a Nucleophile. Reaction of **3** and **4** with amines provided clear evidence for differences in reactivity. The reaction of **3** with aniline, in the presence of triethylamine as a hydrohalide acceptor, yielded the fully substituted trimer **7** after 1 week in dioxane at 102 °C. Under similar conditions, **4** reacted only at the exocyclic P–Cl bonds and no ring substitution was detected. The resultant anilino/fluoro trimer was treated with sodium trifluoroethoxide. A complex mixture of products was formed. Mass spectra indicated the presence of species with more than 5 trifluoroethoxy groups. This suggests that some of the anilino groups were displaced by trifluoroethoxy groups. Mass spectra contained signals that corresponded to mono-, di-, and trianilino products. Removal of the amine hydrochlorides before treatment with a near-stoichiometric amount of sodium trifluoroethoxide still resulted in displacement of aniline.

(d) *n*-Propylamine as a Nucleophile. The reactions of trimers **3** and **4** with *n*-propylamine gave results that were similar to those with aniline. Reaction of **3** with *n*-propylamine in the presence of triethylamine as a hydrochloride acceptor yielded the fully substituted trimer **9**. The product was isolated as a hydrogen chloride adduct. Trimer **4** reacted only at the exocyclic chlorine atoms. By contrast to the reactions of aniline described above, treatment of the product from this reaction with sodium trifluoroethoxide yielded trimer **10** as the sole product. This allows the difference in reactivity between the chloro and fluoro polymers to be assessed without the problem of side group displacement.

(2) Macromolecular Substitution Reactions. It was known from previous work[24] that differences exist between the reactivities of poly(dichlorophosphazene) (**11**) and poly(difluorophosphazene) (**12**) toward various nucleophiles. The classical polyphosphazenes **11** and **12** react completely with sodium trifluoroethoxide and sodium phenoxide to yield fully substituted products. However, polymer **12** reacts with primary or secondary amines (such as NH_2CH_3, $NH_2C_4H_9$, or $NH(CH_3)_2$) to yield only partially substituted polymers.[24] Under suitable reaction conditions all the chlorine atoms in polymer **11** can normally be replaced except in reactions that involve highly hindered nucleophiles such as diethylamine or amino azo dyes.[25,26]

As with classical phosphazenes, substitution in poly(phosphazophosphazenes) **14** and **15** occurred more easily at P–Cl sites than at P–F units. Full substitution of polymer **14** was obtained with both sodium trifluoroethoxide and *n*-propylamine as nucleophiles. Partially substituted, moisture-stable polymers were obtained with aniline and sodium phenoxide. Full substitution of polymer **15** was obtained only with sodium trifluoroethoxide. Reaction of **15** with sodium phenoxide, aniline, and *n*-propylamine yielded polymers with varying amounts of unreacted chlorine. Sodium phenoxide yielded the highest degree of substitution, followed by *n*-propylamine. Aniline was the poorest nucleophile. Hydrolytically stable polymers containing propylamino or anilino side groups were obtained by replacement of the remaining chlorine atoms by sodium trifluoroethoxide.

Table 2. Polymer Characterization Data

compd	^{31}P NMR	^{1}H NMR	^{13}C NMR	M_n, M_w	elem anal.
14	−30 (m), −24 (m) −10 (d, J_{PP} = 19 Hz)	N/A	N/A	*a*	*a*
15	−23.7 (tm, J_{PF} = 939) −21.7 (dm, J_{PF} = 881) −5.5 (m), −7.1 (m)	N/A	N/A	*a*	*a*
16	−4.6 (br s), −5.7 (br s) −11.9 (br s), −12.5 (br s)	4.2 (br s) 4.4 (br s)	62.5 (m, CH_2CF_3) 123.3 (qm, J_{CF} = 216 Hz)	2.6×10^5, 7.6×10^5	calcd C, 19.77; H, 1.66; N, 5.76; F, 46.90 found C, 18.71, H, 1.92; N, 5.91, F, 45.77
17	−31 (br s) −24 (br s)	7.1 (br s) 6.9 (br s)	152.0, 150.5, 150.4, 129.5, 128.6, 125.1, 123.0, 121.5, 120.6, 120.5	2.2×10^5, 7.5×10^5	calcd C, 62.3; H, 4.36; N, 6.06; Cl, 0.00 found C, 56.56; H, 3.77, N, 5.75; Cl 2.99
18	−15 (br s) (−5, −4, −2, sh)	6.8 (br s)	141 (br s), 128 (br s), 118, (br s, sh 120)	1.3×10^5, 3.8×10^5	calcd C, 62.9; H, 5.28; N, 18.3; Cl, 0.00 found C, 57.79; H, 5.53; N, 17.45; Cl, 0.85
19	−17 (br s, −11, sh) −9 (br s), −2 (br s)	4.1 (br, CH_2CF_3) 7.2 (br, aryl)	64 (m, CH_2CF_3) 120, 126, 130, 139, 141	9.4×10^4, 1.2×10^5	calcd C, 35.87; H, 3.01; N, 10.46; Cl, 0.000; F, 29.38 found C, 33.56; H, 2.82; N, 10.27; Cl 0.018; F, 28.46
20	−1.6 (br s) 4.4 (br s) 11.93 (br s)	0.9 (br s, 3H, CH_3) 1.5 (br s, 2H, CH_2CH_3) 2.8 (br s, 2H, NCH_2)	11.7 (CH_3) 25.0 (CH_2CH_3) 43.0 ($NHCH_2$)	1.8×10^4, 8.1×10^4	calcd C, 44.69; H, 10.01; N, 26.07; Cl, 0.00 found C, 41.71; H, 9.75; N, 26.03; Cl, 0.22
21	−6 (br s; −10, sh; −2, sh) 2 (br s; 8 sh) 15 (br s; 18 sh)	0.9 (br s, 3H, CH_3) 1.5 (br s, 2H, CH_2CH_3) 2.8 (br s, 2H, NCH_2) 4.2 (br s, 1.5H, CH_2CF_3)	11.1 (CH_3) 24.7 (CH_2CH_3) 42.8 ($NHCH_2$) 62 (m, CH_2CF_3) 123.8 (q, CF_3, J_{CF} = 271 Hz)	8.5×10^4, 2.7×10^5	calcd C, 31.56; H, 5.61; N, 15.37; Cl, 0.00; F, 24.72 found C, 28.17; H, 4.89; N, 15.02; Cl, 0.015; F, 23.76

[a] Molecular weight and elemental microanalysis data were not obtained due to the hydrolytic instability of these polymers.

Thus, poly(phosphazophosphazene) substitution with alkoxides, aryloxides, and amines proved to be more complex than the substitution reactions of classical phosphazenes. The polymers were characterized by ^{1}H NMR, ^{31}P NMR, ^{13}C NMR, elemental analysis, gel permeation chromatography (GPC), and differential scanning calorimetry (DSC) (see Table 2).

(a) Sodium Trifluoroethoxide as a Nucleophile. Reaction of poly[(trichlorophosphazo)pentachlorophosphazene] (**14**) and poly[(trichlorophosphazo)pentafluorophosphazene] (**15**) with sodium trifluoroethoxide gave fully substituted polymer **16**. The ^{31}P NMR spectrum of **16** revealed the absence of a large P−F coupling and thus was taken as evidence for full substitution. The products from the reaction of the phosphazofluoro- and phosphazochlorophosphazene with sodium trifluoroethoxide were identical at both the cyclic trimeric and the linear high polymeric levels.

(b) Sodium Phenoxide as a Nucleophile. The reaction of sodium phenoxide with **14** and **15** in dioxane at 102 °C for 1 week left approximately one halogen atom per repeat unit unreacted. The use of higher boiling solvents, such as diglyme, or reaction in a pressure vessel resulted in decomposition as evidenced by a broad, undefined peak in the ^{31}P NMR. Full substitution was not achieved even in the presence of tetra-*n*-butylammonium bromide as a phase-transfer reagent. The presence of a bulky aryloxy substituent attached to the ring or chain would retard the replacement of the remaining halogen atoms. The additional bulk of the phosphazo unit would also shield the remaining halogens from the reagent. In the case of **15**, the reaction of the polymer is further complicated by the low reactivity of the fluorine atoms that remain. It is speculated that the unreacted halogen atoms are geminal to the phosphazo unit, as suggested by the trimeric model reaction. The shielding influence of the phenoxy and phenoxyphosphazo groups may also be responsible for the moisture stability of these polymers. Polyphosphazenes that contain phosphorus−halogen bonds are usually sensitive to hydrolysis. However, the polymers produced by the reactions of **14** and **15** with sodium phenoxide showed no evidence of hydrolysis (by ^{31}P NMR) after exposure to water and retained their solubility in organic solvents. This is compatible with the absence of P−OH units that could induce cross-links. The same property was found for the poly(diphosphazophosphazenes) where only the phosphazo chlorine atoms were replaced by bulky organic side groups.[18]

(c) Aniline as a Nucleophile. The treatment of **14** with aniline yielded a water-stable polymer with approximately one unreacted halogen atom per repeat unit remaining. This is similar to the results with sodium phenoxide. The reaction of **15** with aniline gave a partially substituted, moisture-sensitive polymer. Treatment of this polymer with excess sodium trifluoroethoxide yielded a water-stable anilino/trifluoroethoxide mixed-substituent polymer.

A difference in reactivity between trimer **4** and polymer **15** was detected. While no replacement of ring fluorine atoms was detected for the reaction of aniline with **4**, integration of the ^{1}H and ^{31}P NMR spectra and elemental analysis data suggested that aniline had reacted with at least 2% of the main-chain P−F bonds. Thus, the anilino groups are not confined to the phosphazo branch units. As in the model trimer reaction, these results are complicated by the possibility that anilino groups may be displaced by trifluoroethoxy groups during subsequent exposure to sodium trifluoroethoxide. This displacement could occur at the phosphazo units, as seen in the trimer study, or at sites connected directly to the polymer backbone. Attempts to limit the aniline displacement by the use of near-stoichiometric sodium trifluoroethoxide in the polymer reactions were hindered by not knowing the exact amount of anilino groups on the intermediate fluoro/anilino polymer. It is probable that a significant number of anilino groups, at both phosphazo sites and main chain sites, are displaced. Therefore, the anilino/trifluoroethoxy distribution of polymer **19** is complex.

(d) *n*-Propylamine as a Nucleophile. The reaction of poly[(trichlorophosphazo)pentachlorophosphazene] with *n*-propylamine yielded a fully substituted polymer (**20**). It is speculated that the residual chlorine (0.22%) detected in the product polymer is due to the presence of hydrogen chloride coordinated to the polymer, as suggested by the trimeric model reaction. There was no evidence for the presence of residual phosphorus–chlorine bonds in the ^{31}P NMR spectrum. The Lewis-base behavior of hexakis(*n*-alkylamino)cyclotriphosphazenes is well known and has been studied extensively.[27-29] Hydrogen chloride coordination to polyphosphazenes is also known when poly(dichlorophosphazene) is allowed to react with primary or secondary amines.[30]

As with the aniline reaction, a difference was detected in reactivity between trimer **4** and polymer **15**. No ring substitution occurred with trimer **4**. However, poly[(trichlorophosphazo)pentafluorophosphazene] reacted with *n*-propylamine at the phosphazo chlorine atoms as well as at 48% of the backbone P–F sites. The polymer was subsequently treated with an excess of sodium trifluoroethoxide to yield moisture-stable polymer **21**. It should be noted that the degree of initial substitution was greater with *n*-propylamine than with aniline, which may be due to the lower steric constraints imposed by *n*-propylamine. However, it is also possible that a similar level of substitution occurs with aniline and *n*-propylamine but that the difference in the final loading of amino groups is due to the side group displacement of aniline. Neither of the amine reagents yield completely aminolyzed products. The incomplete substitution is not entirely a consequence of steric crowding, since complete or near-complete substitution was achieved with both *n*-propylamine and aniline for the phosphazochloro polymer **14**. Apparently, electron donation from an amino substituent attached to phosphorus deactivates the second phosphorus–fluorine bond at that site. The combined influences of the low nucleophilicity of a free amine and the poor leaving-group ability of the fluoride ion would enhance this effect.

Glass Transition Temperatures. One of the main lines of inquiry in the fundamental science of polyphosphazenes seeks to relate structure with properties. Comparison of the glass transition temperatures (T_g's) of poly(monophosphazophosphazenes), poly(diphosphazophosphazenes), and classical polyphosphazenes provides a way to measure the effects of different side groups, including phosphazo units, on solid-state properties. Previously, a comparison was made of several poly(1,1-diphosphazophosphazenes) with classical polyphosphazenes.[18] A compilation of the T_g data for the polymers in this study and previously synthesized, related polymers is found in Table 3.

(a) Halogenophosphazene Polymers. Poly(difluorophosphazene) (**12**) has a T_g of −96 °C. Introduction of the trichlorophosphazo side unit into this structure did not significantly affect the T_g since polymer **15** had a T_g of −95 °C. Conformational analysis[31] has suggested that polymer **12** can undergo broad conformational changes involving 360° torsion of adjacent skeletal bonds without encountering significant torsional barriers. Presumably the chlorophosphazo unit does not inhibit the high torsional flexibility of the main chain. However, the introduction of one trichlorophosphazo unit per six-atom repeat unit onto the backbone of poly(dichlorophosphazene) (**11**) raised the glass transition temperature from −66 to −41 °C. This T_g is close to that of the poly(1,1-diphosphazophosphazene) (**13**) (T_g of −37 °C). Thus the steric bulk of the phosphazo units appears to hinder the torsional motion of a chlorophosphazene backbone more severely than in the case of a fluoropolymer. Apparently, little difference in the free volume and hindrance to torsional mobility is generated by two trichlorophosphazo units compared to one unit.

Table 3. Glass Transition Temperatures

compd	T_g, °C	compd	T_g, °C	compd	T_g, °C
11	−66	**17**	12	**23**	−6
12	−96	**18**	*a*	**24**	91
13	−37	**19**	37	**25**	4
14	−41	**20**	*a*	**26**	−70
15	−95	**21**	50	**27**	26
16	−12	**22**	−66		

[a] T_g not detected by DSC.

(b) Organosubstituted Polymers. The T_g's of the classical (trifluoroethoxy)phosphazene polymer (**22**) and the diphosphazo trifluoroethoxy counterpart (**26**) are similar (−66 and −70 °C, respectively). This suggests that the flexible fluoroalkoxy side groups in conjunction with the two phosphazo units maintain enough chain flexibility and free volume to yield a material with a virtually unchanged glass transition temperature. Surprisingly, the T_g of the monophosphazo trifluoroethoxy derivative is −12 °C. This striking difference is difficult to rationalize in terms of chain flexibility or free volume arguments, and molecular modeling work is planned to investigate this phenomenon. However, a similar trend is found for polyethylene, polypropylene, and polyisobutylene.[32] The T_g of polyethylene has been given as −30, −80, and −128 °C. The addition of one methyl group to polyethylene to yield polypropylene raises the T_g to −17 °C. The addition of a second methyl group, to yield polyisobutylene, lowers the T_g to −73 °C.

In the case of the aryloxy-substituted polymers, the effects of bulky substituents on backbone flexibility are more pronounced and follow a more logical sequence. The classical poly(diphenoxyphosphazene) (**23**) has the lowest T_g (−6 °C) in the series. The addition of one bulky triphenoxyphosphazo group per six skeletal atom repeat units in polymer **17** increased the T_g to +12 °C. Poly[(diphosphazophenoxy)phosphazene] (**27**) has a T_g of +26 °C.

Less direct comparisons could be made for the amino-substituted classical polyphosphazenes and poly(monophosphazophosphazenes). Poly(dianilinophosphazene) (**24**) has a T_g of 91 °C.[33] The T_g's of poly[(anilinophosphazo)phosphazene] (**18**) and poly[(propylamino)phosphazo)phosphazene] (**20**) were not detected by DSC analyses. However, polymer **19**, with both anilino and trifluoroethoxy side groups, has a T_g of 37 °C. Although this transition temperature is lower than that of polymer **24**, it is significantly higher than the T_g of −66 °C for polymer **22**, poly[bis(trifluoroethoxy)phosphazene]. Thus, it is inferred that introduction of bulky anilinophosphazo groups produces a significant stiffening of the polymer chain despite the presence of the trifluoroethoxy cosubstituent groups. Polymer **21**, which contained both propylamino and trifluoroethoxy groups, had a T_g of 50 °C. Again, the presence of propylamino and (propylamino)phosphazo side units raised the T_g compared to polymer **22**. Poly[bis(propylamino)phosphazene] (**25**) has a T_g of 4 °C.[25]

In theory, the introduction of short branches into the polymer structure would be expected to generate free volume and thus lower the glass transition temperature. However, in most cases, the phosphazo groups are sufficiently bulky that they hinder the torsional mobility of the polymer backbone. Thus, in general, the monophosphazophosphazenes yield materials with significantly higher T_g's than classical polyphosphazenes. The comparison with diphosphazophosphazenes is more complicated. The (trifluoroethoxy)monophosphazophosphazene has a higher glass transition temperature than the corresponding diphosphazo polymer. However, the (aryloxy)monophosphazo polymer has a lower glass transition temperature.

As with classical phosphazenes, the properties of the polymers are greatly influenced by the choice of side group. In the phosphazophosphazene series, contributions to the free volume, which can lower the T_g, compete with the effects of steric bulk, which can hinder the torsional mobility of the polymer backbone and raise the T_g.

Conclusions

In this work, we have shown that trichloromonophosphazo trimers **3** and **4** undergo thermal ring-opening polymerization to form polyphosphazenes with $N{=}PX_3$ side groups. These polymers are able to undergo nucleophilic substitution to obtain moisture-stable polymers and also provide opportunities for regioselective substitution processes. It was more difficult to obtain full substitution on the fluoropolymer **15** than with chloropolymer **14**. Finally, the glass transition temperatures could be tuned over a wide range by variations in the type of organic side groups employed.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**) was supplied by Ethyl Corp. and was purified by one recrystallization from heptane and two vacuum sublimations at 0.05 Torr. Phenol (Aldrich) was purified by vacuum sublimation before use. Sodium (Aldrich), sodium hydride (60% dispersion in mineral oil, Aldrich), phosphorus pentachloride (Aldrich), and ammonia (anhydrous, Liquid Carbonic) were used as received. 2,2,2-Trifluoroethanol (Halocarbon) was distilled from anhydrous $CaSO_4$ and was stored over 4 Å molecular sieves. Aniline (Aldrich) was distilled from barium oxide and was stored shielded from light. *n*-Propylamine was distilled from barium oxide and was stored, in the dark, over 4 Å molecular sieves. 1,4-Dioxane (Aldrich, anhydrous) and tetrahydrofuran were distilled into the reaction flask from sodium–benzophenone ketyl in an atmosphere of dry argon or nitrogen. Heptane, dichloromethane, and triethylamine (Baker) were dried and distilled from CaH_2 into the reaction flask in an atmosphere of dry argon or nitrogen. All glassware was dried overnight in an oven or flame dried under vacuum before use. The reactions were performed using standard Schlenk techniques utilizing an atmosphere of dry argon.

Equipment. ^{31}P NMR spectra were recorded with the use of a JEOL FX90Q NMR spectrometer operated at 36.2 MHz or with a Bruker WM-360 NMR spectrometer at 146 MHz. ^{31}P chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. ^1H and ^{13}C NMR spectra were recorded with a Bruker WM-360 NMR spectrometer operated at 360 and 90.27 MHz, respectively. ^1H and ^{13}C NMR spectra are referenced to internal $CDCl_3$ or acetone-d_6. Elemental microanalyses were obtained by Galbraith Laboratories, Knoxville, TN. Molecular weights were estimated using a Hewlett-Packard HP1090 gel permeation chromatograph equipped with an HP-1037A refractive index detector and a Polymer Laboratories PL Gel 10 μm column. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF (OmniSolv). The GPC column was calibrated with polystyrene standards (Waters) and with fractionated samples of poly[bis(trifluoroethoxy)phosphazene] provided by Drs. R. Singler and G. Hagnauer of the U.S. Army Materials Technology Laboratories, Watertown, MA. Glass transition temperatures were obtained by differential scanning calorimetry using a Perkin-Elmer DSC-7 unit controlled by a PE7500 computer. Heating rates of 10–25 °C/min and a sample size of 15–30 mg were used.

Synthesis of Cyclic Trimers $N_3P_3Cl_5NPCl_3$ (3) and $N_3P_3F_5NPCl_3$ (4). The preparation of trimers **3** (12 g, 75% yield) and **4** (10 g, 92% yield) followed procedures reported in the literature.[34,35]

Synthesis of Cyclic Trimer $N_3P_3(OCH_2CF_3)_5NP(OCH_2CF_3)_3$ (5). $N_3P_3Cl_5NPCl_3$ (**3**) (2.0 g, 4.3 mmol) or $N_3P_3F_5NPCl_3$ (**4**) (2.0 g, 5.2 mmol) in freshly distilled dioxane (50 mL) was added dropwise to a solution of sodium trifluoroethoxide (1.3 g, 56 mmol of Na;[36] 3.9 g, 39 mmol of trifluoroethanol) in dioxane (150 mL). The reaction mixture was heated to reflux for 24 h. The product was isolated by filtration through Fuller's earth and was concentrated by rotary evaporation. The product was dissolved in diethyl ether (250 mL), washed with water (3 × 100 mL), dried over $MgSO_4$, and concentrated by rotary evaporation to yield a brown oil. Final purification was by column chromatography on silica gel using hexane and methylene chloride as eluents or by vacuum distillation (109–110 °C, 10 μm) and yielded a clear, colorless oil (68% yield). FABS-MS: calcd MI = 972, found MH^+ = 973.

Synthesis of Cyclic Trimer $N_3P_3(OC_6H_5)_5NP(OC_6H_5)_3$ (6). $N_3P_3Cl_5NPCl_3$ (**3**) (2.0 g, 4.3 mmol) in freshly distilled dioxane (50 mL) was added dropwise to a solution of sodium phenoxide (1.7 g, 43 mmol of NaH; 3.9 g, 41 mmol of phenol) in dioxane (150 mL). The reaction mixture was heated to reflux for 48 h. The product was isolated by filtration through Fuller's earth and was concentrated by rotary evaporation. The product was dissolved in diethyl ether (250 mL) and was washed with 10% NaOH (3 × 100 mL), dried over $MgSO_4$, and concentrated by rotary evaporation to yield a brown oil. Final purification was by column chromatography through silica gel using hexane and methylene chloride as eluents to yield a clear, slightly yellow oil from which colorless crystals were obtained (mp 65–67 °C, uncorrected) (54% yield). FAB-MS: calcd MI = 924, found MH^+ = 925.

The analogous reaction with the fluoro trimer **4** gave a mixture of monofluoro- and difluorophenoxy-substituted trimers after refluxing in dioxane at 102 °C for 1 week. The mixture was inseparable by column chromatography. FAB-MS: calcd MI = 924, found MH^+ = 851 ($N_3P_3F(OC_6H_5)_4NP(OC_6H_5)_3$) and MH^+ = 777 ($N_3P_3F_2(OC_6H_5)_3NP(OC_6H_5)_3$).

Synthesis of Cyclic Trimer $N_3P_3(NHC_6H_5)_5NP(NHC_6H_5)_3$ (7). $N_3P_3Cl_5NPCl_3$ (**3**) (3.0 g, 6.5 mmol) in dioxane (20 mL) was added dropwise to a solution of aniline (9.6 g, 0.1 mol) and triethylamine (5.2 g, 51 mmol) in dioxane (150 mL). The reaction mixture was heated to reflux for 4 days. The mixture was filtered through a fritted funnel and most of the solvent was removed by vacuum. Diethyl ether was added to precipitate the compound. The suspension was centrifuged and the brown ethereal layer was removed by pipet. The purification was repeated twice. Removal of the residual ether in vacuum yielded a white powder (mp 217 °C, uncorrected) (40% yield). FAB-MS: calcd MI = 916, found MH^+ = 917.

Synthesis of Cyclic Trimer $N_3P_3(OCH_2CF_3)_5NP(OCH_2CF_3)_x(NHC_6H_5)_{3-x}$ (8). Trimer **4** (1.08 g, 2.83 mmol) in toluene (25 mL) was added dropwise to a solution of aniline (64.6 g, 69.4 mmol) in triethylamine/toluene (10 mL/50 mL). The reaction mixture was heated to reflux for 3 days. The mixture was filtered through Fuller's earth, concentrated, and dried under vacuum (2 days). The resulting brown oil was dissolved in THF (50 mL) and was added dropwise to a solution of sodium trifluoroethoxide (0.58 g, 25.2 mmol of Na; 2.75 g, 27.5 mmol of trifluoroethanol) in THF (50 mL). The reaction mixture was then refluxed overnight, filtered through Fuller's earth, and concentrated. A mixture of products was obtained that was inseparable by column chromatography. MS indicated $x = 0-2$. EI-MS: calcd MI = 951, found M^+ = 951, 958, 965.

Synthesis of Cyclic Trimer $N_3P_3(NHC_3H_7)_5NP(NHC_3H_7)_3$ (9). Trimer **3** (4.5 g, 9.7 mmol) in toluene (100 mL) was added dropwise to a solution of *n*-propylamine (13.7 g, 232 mmol) in toluene (150 mL). The reaction mixture was heated to reflux for 3 days. The precipitated salts were then removed by centrifugation. The supernatant liquid was decanted and concentrated to obtain a yellow oil. The oil was purified by column chromatography using alumina as the stationary phase and methanol as the eluent. The clear, colorless oil crystallized on standing to form clear, colorless crystals. The product was isolated as a hydrogen chloride adduct (mp 89–90 °C, uncorrected) (61% yield). EI-MS: calcd MI = 644, found M^+ = 644.

Synthesis of Cyclic Trimer $N_3P_3(OCH_2CF_3)_5NP(NHC_3H_7)_3$ (10). Trimer **4** (0.60 g, 1.57 mmol) in THF (10 mL) was added dropwise to a solution of *n*-propylamine (2.70 g, 45.6 mmol) in THF (50 mL). The solution was heated to reflux for 4 h. Sodium trifluoroethoxide (1.1 g, 28 mmol of NaH; 2.5 g, 25 mmol of trifluoroethanol) in THF (50 mL) was added to the cooled solution through a fritted addition funnel. The reaction mixture was heated to reflux for 12 h. The product was isolated by filtration through Fuller's earth and concentration by rotary evaporation. The product was dissolved in diethyl ether (250 mL), washed with water (3 × 100 mL), dried over $MgSO_4$, and concentrated by rotary evaporation to yield a brown oil. Final purification was by crystallization from hexane at −55 °C to obtain white crystals (mp 44–45 °C, uncorrected) (41% yield). FAB-MS: calcd MI = 849, found MH^+ = 850.

Synthesis of Polymer $[N_3P_3Cl_5NPCl_3]_n$ (14). (Trichlorophosphazo)pentachlorocyclotriphosphazene (**3**) (4.0 g, 8.6 mmol) was melted and sealed in an evacuated, thick-walled glass tube. The trimer was heated for 2 h at 150 °C and 6–8 h at 180 °C until the contents became viscous and slightly brown. The tube was opened under argon and the contents were dissolved in methylene chloride. The moisture-sensitive polymer was purified by the addition of heptane to a concentrated solution of the polymer in methylene chloride. This procedure was carried out three times to yield a white, elastomeric material. This polymeric intermediate (**14**) was used immediately in nucleophilic substitution reactions. A typical polymerization yield of 60–70% was obtained as estimated by ^{31}P NMR analysis.[37]

Synthesis of Polymer $[N_3P_3F_5NPCl_3]_n$ (15). (Trichlorophosphazo)pentafluorocyclotriphosphazene (**4**) (2.0 g, 5.2 mmol) was sealed under vacuum in a thick-walled glass tube. The tube contents were heated at 210 °C until the contents were almost immobile (2–24 h depending of different batches of the trimer). The moisture-sensitive product was purified by the addition of heptane to a concentrated solution of the polymer in methylene chloride. This procedure was carried out three times to yield a white, elastomeric material. This polymeric intermediate (**15**) was used immediately in nucleophilic substitution reactions. A typical polymerization yield of 60–70% was obtained as estimated by ^{31}P NMR analysis.

Synthesis of Polymer $[N_3P_3(OCH_2CF_3)_5NP(OCH_2CF_3)_3]_n$ (16). Polymer **14** or **15** (approximately 2 g, 4.3 or 5.2 mmol/*n*, respectively) was dissolved in dioxane (250 mL) and added to sodium trifluoroethoxide (1.57 g, 68.3 mmol of Na; 8.28 g, 82.8 mmol of trifluoroethanol) in dioxane (100 mL). The reaction mixture was heated at reflux for 16 h and was then concentrated by rotary evaporation. The polymer was precipitated from a viscous solution in THF into distilled water (3×) and into hexane (1×) to yield a white, flexible material.

Synthesis of Polymer $[N_3P_3(OC_6H_5)_5NP(OC_6H_5)_3]_n$ (17). Polymer **14** or **15** (approximately 2.2 g, 4.7 or 5.8 mmol/*n*, respectively) in toluene (100 mL) was added dropwise to sodium phenoxide (3.36 g, 140 mmol of NaH; 13.17 g, 140 mmol of phenol) in dioxane (125 mL). The reaction mixture was heated to reflux at 102 °C for 1 week. The solution was then concentrated by rotary evaporation. The polymer was precipitated from a viscous solution in THF into distilled water (3×) and into hexane (1×) to yield a white, flexible polymer.

Synthesis of Polymer $[N_3P_3(NHC_6H_5)_5NP(NHC_6H_5)_3]_n$ (18). Polymer **14** (approximately 2.2 g, 4.7 mmol/*n*) in dioxane (100 mL) was added dropwise to aniline (12.3 g, 0.131 mol) in a mixture of triethylamine (30 mL) and dioxane (70 mL). The reaction mixture was heated to reflux and was stirred for 1 week. The polymer was precipitated from this mixture into water and into hexane several times to yield a tan powder.

Synthesis of Polymer $[N_3P_3(OCH_2CF_3)_5NP(NHC_6H_5)_3]_n$ (19). Polymer **15** (approximately 1.5 g, 3.9 mmol/*n*) in toluene (100 mL) was added to a solution of aniline (7.15 g, 76.5 mmol) in toluene (20 mL). The reaction mixture was heated to reflux for 48 h. Sodium trifluoroethoxide was then prepared by the addition of trifluoroethanol (3.77 g, 37.7 mmol) in THF (50 mL) to a suspension of NaH (1.66 g, 37.8 mmol) in THF (50 mL). The polymer/aniline reaction mixture was added dropwise to sodium trifluoroethoxide (3.77 g, 37.7 mmol; 1.66 g, 37.8 mmol of NaH) in THF (100 mL), and the reaction mixture was heated to reflux for 48 h. The polymer was purified by precipitation from THF into water (3×) and hexane (1×) and finally by dialysis against methanol to yield a white, powdery material.

Synthesis of Polymer $[N_3P_3(NHC_3H_7)_5NP(NHC_3H_7)_3]_n$ (20). Polymer **14** (approximately 1.0 g, 2.2 mmol/*n*) in toluene (100 mL) was added to a mixture of *n*-propylamine (2.0 g, 3.4 mmol) and triethylamine (7.3 g, 0.0717 mol). The reaction mixture was heated to reflux for 4 days. The reaction mixture was then dialyzed against deionized water (4 days) and ethanol (6 days). The ethanol was removed by rotary evaporation to yield an off-white powder.

Synthesis of Polymer $[N_3P_3(OCH_2CF_3)_{2.6}(NHC_3H_7)_{2.4}NP(NHC_3H_7)_3]_n$ (21). Polymer **15** (approximately 2.5 g, 6.6 mmol/*n*) in toluene (120 mL) was added to *n*-propylamine (14.4 g, 0.24 mol) in toluene (20 mL). The polymer/*n*-propylamine reaction mixture was added dropwise to sodium trifluoroethoxide (5.04 g, 0.13 mol of NaH; 13.75 g, 0.14 mol of trifluoroethanol) in THF (250 mL). The polymer was purified by precipitation from THF into water (3×) and hexane (1×) and finally by dialysis against methanol to yield a white, flexible material.

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(36) Excess sodium metal was employed to ensure the absence of residual CF_3CH_2OH, which can act as a proton source and lead to side reactions. Thus, this is a precautionary step and not an absolute necessity.

(37) Polymers **14** and **15** were not isolated in the dry state. Hence, the 60–70% yields given are approximate. Conversion of **14** and **15** to substituted products was 100%, but polymer purification reduced the overall yield of isolated polymer to 50–70% based on **14** and **15**. Hence, the overall yields based on the starting cyclic trimers were 30–50%.