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Functionalized Polyphosphazenes: Polymers with Pendent Tertiary Trialkylamino Groups

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ABSTRACT: Attempts have been made to synthesize polyphosphazenes with pendent tertiary amino side units via macromolecular substitution. Incorporation of $-OCH_2CH_2N(CH_3)_2$, $-OCH_2CH_2OCH_2CH_2N(CH_3)_2$, and $-NHCH_2CH_2N(CH_3)_2$ groups was studied. Polymers in which all the side groups consisted of one type of aliphatic tertiary amino-containing unit and species that also contained 2,2,2-trifluoroethoxy or phenoxy groups as cosubstituents were examined. Related phosphazene cyclic trimers were also prepared as small molecule model systems to examine synthetic variables, characterization techniques, and hydrolytic behavior. Those phosphazenes in which the tertiary amino-containing side groups are linked to the skeleton through an aliphatic oxygen−phosphorus bond are sensitive to hydrolysis induced by the basicity of the terminal amino group. However, species in which the tertiary amino-containing units are linked to the backbone through an alkyl nitrogen−phosphorus bond are stable to water and are candidate materials for use in a range of membrane and surface applications. Small molecule model studies also identified reactions of P−Cl bonds in $(NPCl_2)_3$ with *N*,*N*-dimethylbutylamine to form dialkylamino-substituted phosphazenes and hydrolysis products.

Introduction

Polymers with aliphatic or aromatic tertiary amino groups are of interest for a variety of reasons. The hydrophilicity and basicity of some tertiary amino groups can increase the solubility of polymers in neutral or acidic aqueous media. The tertiary amino group can also form complexes with metal cations. In addition, such groups react with acids or alkyl halides to form amine hydrohalide or alkyl quaternary ammonium salts. For these reasons, classical organic polymers with tertiary amino groups or quaternized functionalities are widely used as anion-exchange resins, flocculants, antistatic agents, biocides, and membranes.[1−9] In particular, poly(vinylpyridinium) salts and poly(acrylamides) with pendent quaternary ammonium groups have been studied in detail for these applications.[1,4−9]

Polyphosphazenes comprise a broad, versatile class of macromolecules with the general formula $(NPR_2)_n$ in which the side groups R may be any of a wide variety of alkyl, aryl, amino, alkoxy, aryloxy, or organometallic units.[10−12] The structural versatility of phosphazenes is a consequence of the methods used to prepare these materials. In the most widely used synthetic pathway, poly(dichlorophosphazene), $(NPCl_2)_n$ (**2**), is first produced via the thermal ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**). The polymer can also be prepared with a narrow molecular weight distribution by a recently developed living, cationic polymerization of a chlorophosphoranimine.[13,14] Poly(dichlorophosphazene) then serves as a macromolecular intermediate for chlorine replacement reactions when treated with a wide range of nucleophiles to yield high molecular weight polymers with organic or organometallic side groups.

The properties of polyphosphazenes can be understood in terms of a highly flexible inorganic backbone with additional physical and chemical characteristics imposed by the organic side group structure.[10,15−17a] In particular, the side groups strongly influence polymer solubility, membrane behavior, surface character, and stability to chemical reagents. Compared to other polymer systems that bear tertiary amino groups, polyphosphazenes offer the potential advantage of fine control over both the bulk properties and the surface character in ways that can be difficult to accomplish with conventional organic macromolecules. This is due to the large number of side groups that can be easily incorporated into the polymer structure in varying ratios in order to tailor polymer properties for specific applications.

A wide range of nitrogen-functionalized phosphazenes have been designed and synthesized in recent years. These incorporate primary alkyl- or arylamines, imidazole, isothiocyanates, thiourethanes, thioureas, pyrrole, or pyridine side units.[18−25] However, phosphazenes with aliphatic tertiary amines, specifically $-OCH_2CH_2N(CH_3)_2$, in the side group structure have been limited to mixed-substituent materials with less than 20% of the side groups bearing the tertiary amine, and this undoubtedly disguised some of the problems that became apparent in the present work.[26,27]

The incorporation of tertiary amino units into the side groups of polyphosphazenes can, in principle, be accomplished through reaction of a chlorophosphazene such as **2** with an alkoxide, aryloxide, primary amine, or secondary amine that bears a tertiary amino residue, typically at the terminus of the reagent. However, earlier work implied that the reactions of chlorophosphazenes with reagents that contain tertiary amino units can be complex. For example, pyridine reacts with small molecule chlorophosphazenes to produce “addition compounds” that are extremely reactive toward water.[28] Trimethylamine has also been found to react with **1** to produce aminophosphazenes.[29] Furthermore, because tertiary amines act as bases toward hydrogen chloride, conventional synthetic routes to organophosphazenes may produce polymers in which the tertiary amino sites are converted to their amine hydrochloride salts. These

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Chart 1. Target Polymers with Tertiary Amino Side Units

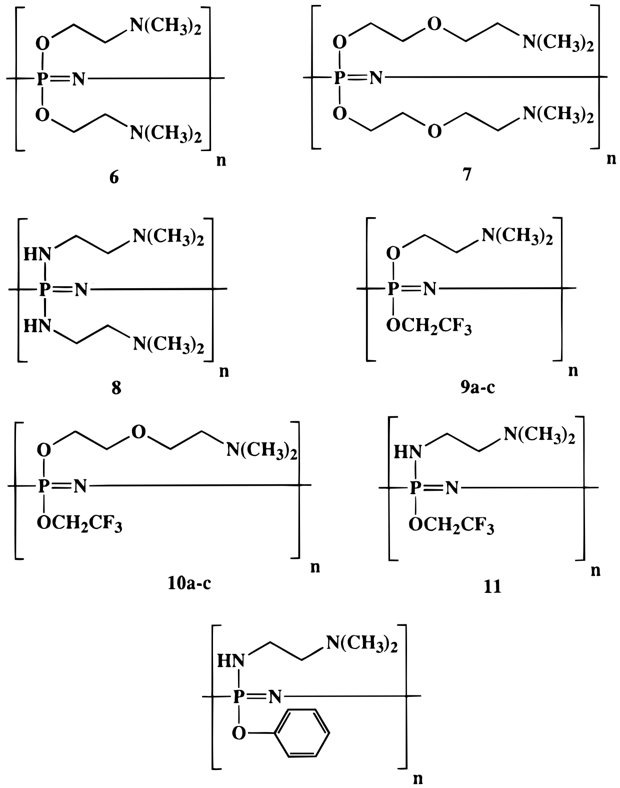
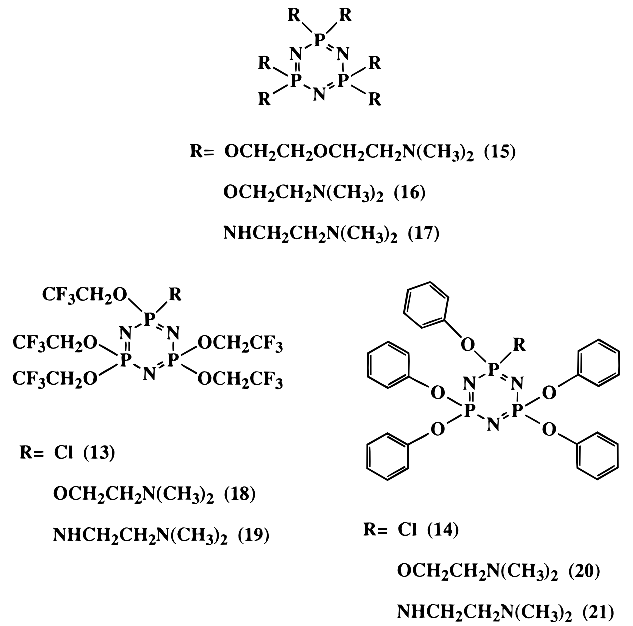


Chart 2. Model Compounds for the Synthesis Studies



salts are insoluble in most of the organic solvents that are appropriate for phosphazene substitution reactions, and their presence can lead to precipitation of the polymer before complete chlorine replacement has occurred. The remaining P−Cl bonds are sites of hydrolytic instability and could eventually lead to polymer degradation.

The objectives in this study were to determine if any underlying chemical reasons exist why polymers with high loadings of pendent aliphatic tertiary amino groups cannot be prepared and to examine the influence of the tertiary amino groups on phosphazene properties. To our knowledge, fully substituted phosphazenes of types **6**−**8** (Chart 1) and mixed-substituent species such as **9**−**12** (Chart 1) with high loadings of an aliphatic tertiary amine had not been prepared.

A reason for our interest in these polymers was their possible behavior as membrane and surface active materials. The presence of hydrophobic $-OCH_2CF_3$ and $-OC_6H_5$ cosubstituent groups in **9**−**12** offered the possibility of controlled amphiphilic character.

To gain a better initial insight into the synthetic pathways, attempts were first made to prepare model single-substituent and mixed-substituent cyclic trimer derivatives (**15**−**21**) listed in Chart 2.

A study was also performed on certain cyclic trimer model derivatives (**20**, **21**) to determine the hydrolytic stability of these materials under neutral, acidic, and basic conditions. In addition, because several tertiary amines have been reported to react with chlorophosphazenes to form aminophosphazenes or hydrolytically sensitive derivatives, the interaction of *N*,*N*-dimethylbutylamine with **1** and **14** was examined.

Results and Discussion

Small Molecule Model Compound Syntheses. The synthesis of poly(organophosphazenes) via the macromolecular substitution route requires that an average of ~30 000 chlorine atoms per chain be replaced by organic groups. The success of this process depends on the efficiency of the substitution reaction and particularly on the absence of side reactions. For example, side reactions that lead to phosphorus−nitrogen backbone bond cleavage or premature cross-linking can have serious consequences. However, the fact that several hundred different stable polyphosphazenes have been produced by this process is an indication that most nucleophilic reagents react cleanly with poly(dichlorophosphazene). Nevertheless, some evidence exists from earlier work that reagents that bear tertiary amino units may initiate side reactions, and also that some phosphazenes with tertiary amino units in the side group structure may be sensitive to water. Thus, a need existed to examine these reactions at the small molecule level first before undertaking the more complex macromolecular substitutions.

An initial model reaction study was made of the interactions of $(NPCl_2)_3$ (**1**), $N_3P_3(OCH_2CF_3)_5Cl$ (**13**), and $N_3P_3(OC_6H_5)_5Cl$ (**14**) with $NaOCH_2CH_2N(CH_3)_2$, $NaOCH_2CH_2OCH_2CH_2N(CH_3)_2$, or $NH_2CH_2CH_2N(CH_3)_2$. The structures of the resultant cyclic trimers were examined by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, FAB mass spectrometry, and elemental microanalysis (Table 1).

The fully substituted trimer $[NP(OCH_2CH_2OCH_2CH_2N(CH_3)_2)_2]_3$ (**15**) was obtained by treatment of **1** with $NaOCH_2CH_2OCH_2CH_2N(CH_3)_2$ in tetrahydrofuran (THF). Complete chlorine replacement was indicated by a singlet resonance at 18.6 ppm in the ^{31}P NMR spectrum. The trimer was isolated as a clear, yellow oil through liquid−liquid extraction with chloroform. By contrast, attempts to prepare $[NP(OCH_2CH_2N(CH_3)_2)_2]_3$ by the reaction of either $NaOCH_2CH_2N(CH_3)_2$ or $HOCH_2CH_2N(CH_3)_2$ with **1** failed to yield the target compound (**16**). The insolubility of the sodium salt favored the formation of only partially substituted products, and the use of the free alcohol initially yielded a hexasubstituted product (NMR singlet at 19 ppm), which failed to survive the purification procedure. The possibility exists that this compound is susceptible to rearrange-

Table 1. Cyclic Trimer Characterization Data

trimer	^{31}P (ppm)	^{13}C (ppm)	^{1}H (ppm)	FAB-MS (*m*/*z*)	Anal. Calcd (found)
15	18.6	45.9, 58.9, 65.0, 69.4, 69.8	2.25 (s, 6H), 2.48 (t, 2H), 3.57 (t, 2H), 3.65 (t, 2H), 4.04 (br, 2H)	$MH^+ = 928$	C: 46.60% (46.10%) H: 9.06% (8.89%) N: 9.06% (9.13%) Cl: 0.00% (705 ppm)
17	19.6	38.4, 45.2, 60.4	2.17 (s, 6H), 2.35 (t, 2H), 2.72 (t, 1H), 2.96 (br, 2H)	$MH^+ = 658$	C: 43.81% (43.64%) H: 10.13% (10.06%) N: 31.94% (31.63%) Cl: 0.00% (676 ppm)
19	20.1 (t), 15.2 (d)	37.8, 44.8, 58.7, 62.2 (m), 122.5 (q)	2.09 (s, 6H), 2.13 (t, 2H), 2.68, (br, 2H), 3.22 (br, 1H), 4.11−4.31 (m, 10H)	$MH^+ = 718$	C: 23.44% (23.49%) H: 2.96% (3.09%) N: 9.77% (9.66%) F: 39.73% (39.13%) Cl: 0.00% (944 ppm)
21	18.4 (t), 9.4 (d)	37.7, 44.9, 59.0, 124.2, 124.6, 129.3, 151.0	2.09 (s, 6H), 2.14 (t, 2H), 2.69 (m, 2H), 3.22 (br, 1H), 6.93−7.25 (m, 25H)	$MH^+ = 688$	C: 59.38% (59.75%) H: 5.29% (5.51%) N: 10.19% (10.03%) Cl: 0.00% (53 ppm)

ment to a phospha*zane*, as reported by earlier investigators for cyclic trimers with methoxy or ethoxy side groups.[17b] Cyclic trimer **17** was synthesized by treatment of $(NPCl_2)_3$ with an excess of $NH_2CH_2CH_2N(CH_3)_2$. Full substitution was indicated by a singlet resonance at 19.5 ppm in the ^{31}P NMR spectrum. This trimer is a hygroscopic solid that is soluble in and stable to water.

A simplified model system analogous to the mixed-substituent high polymers was also devised. In this, attempts were made to prepare the pentaphenoxy and pentakis(2,2,2-trifluoroethoxy) cosubstituent cyclic trimers by treatment of $N_3P_3(OCH_2CF_3)_5Cl$ (**13**) or $N_3P_3(OC_6H_5)_5Cl$ (**14**) with $NaOCH_2CH_2N(CH_3)_2$, $NaOCH_2CH_2OCH_2CH_2N(CH_3)_2$, or $NH_2CH_2CH_2N(CH_3)_2$. The pentaphenoxy derivative **20** was obtained through a previously reported synthesis.[26] Species **13** was prepared by the interaction of a 1:5 ratio of **1** with $NaOCH_2CF_3$, a process that was complicated by simultaneous formation of the hexasubstituted derivative, $[NP(OCH_2CF_3)_2]_3$, which could not be removed completely from **13**. Furthermore, attempts to prepare $N_3P_3(OCH_2CF_3)_5(OCH_2CH_2N(CH_3)_2)$ (**18**) were frustrated by the ability of $NaOCH_2CH_2N(CH_3)_2$ to displace trifluoroethoxy groups from phosphorus. This displacement occurred even when this reagent reacted with $[NP(OCH_2CF_3)_2]_3$ that was present as an impurity. The reaction mixtures yielded multiple singlet, doublet, and triplet resonances in the ^{31}P NMR spectrum near 18 ppm. Replacement of trifluoroethoxy groups by other nucleophiles has been reported in previous work.[17c] This displacement reaction was a warning that the same process might also occur at the high polymer level. The results also indicated a possible alternative route to mixed-substituent polymers through treatment of $[NP(OCH_2CF_3)_2]_n$ with the tertiary amine alkoxide.

No displacement of trifluoroethoxy groups was detected when **13** reacted with $NH_2CH_2CH_2N(CH_3)_2$ to produce $N_3P_3(OCH_2CF_3)_5(NHCH_2CH_2N(CH_3)_2)$ (**19**) and unchanged $[NP(OCH_2CF_3)_2]_3$. The structure of **19** was indicated by a doublet (15.2 ppm) and triplet (20.1 ppm) in the ^{31}P NMR spectrum. Due to the hydrophilic character of the amino groups, **19** was easily separated from the $[NP(OCH_2CF_3)_2]_3$ impurity through column chromatography and was obtained as a clear liquid. The pentaphenoxy derivative **21** was prepared through treatment of $N_3P_3(OC_6H_5)_5Cl$ with $NH_2CH_2CH_2N(CH_3)_2$. Analysis of the product showed a clean ^{31}P NMR spectrum consisting of a doublet (9.4 ppm) and triplet (18.4 ppm). Column chromatography produced **21** as a clear oil, which solidified to a white solid when dried under vacuum.

Thus, a conclusion from these small molecule reaction studies is that the synthesis of phosphazene single-substituent polymers with $-OCH_2CH_2N(CH_3)_2$ side units could present problems but that the other two single-substituent polymers might be accessible. The model work also suggested that the displacement of $-OCH_2CF_3$ side groups by $NaOCH_2CH_2N(CH_3)_2$ could complicate the synthesis of mixed-substituent polymers with these two types of side groups. However, mixed-substituent derivatives with $-NHCH_2CH_2N(CH_3)_2$ cosubstituents should be readily accessible with little or no displacement of trifluoroethoxy or phenoxy groups.

Synthesis of Single-Substituent High Polymers. The method of polymer synthesis involved treatment of polymeric intermediate **2** with the sodium alkoxide or amine nucleophiles in 1,4-dioxane as the reaction solvent. However, the preparation of species **6** was more successful when the free alcohol was used rather than the sodium salt. The polymer structures were characterized by ^{31}P, ^{13}C, and ^{1}H NMR spectroscopy, elemental microanalysis, and differential scanning calorimetry (Table 2).

The interaction of $(NPCl_2)_n$ with $NaOCH_2CH_2OCH_2CH_2N(CH_3)_2$ yielded the fully substituted high molecular weight polymer, $[NP(OCH_2CH_2OCH_2CH_2N(CH_3)_2)_2]_n$ (**7**). Complete chlorine replacement was suggested by a ^{31}P NMR spectrum of the reaction mixture, which showed a singlet resonance at −7.8 ppm. However, two broad resonances were also detected at −4 and −7 ppm. Such features in the ^{31}P NMR spectrum of phosphazenes near 0 ppm are often indicative of hydrolysis; however, they could also indicate the presence of phospha*zane* units generated by alkoxy group rearrangement or aminolysis products from reaction of the tertiary amino group with the phosphazene backbone.[17b,30,31] These resonances were detected from the reaction mixture before it was exposed to the atmosphere or to water, and it seems unlikely that they represent the presence of P−OH groups or phosphates derived from unreacted P−Cl units. Furthermore, ^{1}H NMR spectroscopy showed no evidence for the presence of hydroxyl protons or protonated tertiary amino groups. In any event, the broad ^{31}P NMR resonances disappeared when the polymer was purified by dialysis in methanol or THF.

In the preparation of $[NP(OCH_2CH_2N(CH_3)_2)_2]_n$ (**6**), the direct treatment of $(NPCl_2)_n$ with $HOCH_2CH_2N$-

Table 2. Characterization Data for Polymers

polymers	^{31}P (ppm)[b]	^{13}C (ppm)	^{1}H (ppm)	Anal. Calcd (found)
6[a]	−8.6	48.0, 60.5, 65.5	2.25 ($N(CH_3)_2$), 2.57 (CH_2N), 4.00 ($POCH_2$)	C: 43.30% (43.87%) H: 9.07% (8.79%) N: 18.92% (19.83%) Cl: 0.00% (135 ppm)
7[a]	−7.8	48.0, 59.9, 67.5, 69.8, 73.2	2.30 ($N(CH_3)_2$), 2.58 (CH_2N), 3.60 (CH_2OCH_2), 4.05 ($POCH_2$)	C: 46.60% (46.27%) H: 9.06% (8.02%) N: 13.59% (13.29%) Cl: 0.00% (296 ppm)
9a[a]	−7.0	47.0, 61.5, 64.5, 65.1, 124.1	2.30 ($N(CH_3)_2$), 2.51 (CH_2N), 4.16 ($POCH_2$), 4.54 (OCH_2CF_3)	C: 37.09% 36.36%) H: 7.11% (6.86%) N: 15.52% (14.04%) Cl: 0.00% (622 ppm) F: 12.82% (9.46%)
9b[a]	−7.5	48.2, 60.8, 64.2, 65.3, 123.7	2.36 ($N(CH_3)_2$), 2.60 (CH_2N), 4.20 ($POCH_2$), 4.54 (OCH_2CF_3)	C: 31.04% (31.06%) H: 5.21% (5.20%) N: 15.45% (15.60%) Cl: 0.00% (885 ppm) F: 24.55% (22.70%)
9c[a]	−6.8	48.3, 60.2, 64.5, 66.0, 124.2	2.30 ($N(CH_3)_2$), 2.51 (CH_2N), 4.16 ($POCH_2$), 4.45 (OCH_2CF_3)	C: 28.20% (27.86%) H: 3.97% (4.73%) N: 8.22% (8.34%) Cl: 0% (0.15%) F: 32.15% (33.17%)
10a[a]	−7.3	48.0, 59.9, 64.1, 67.5, 69.8, 73.2, 123.7	2.28 ($N(CH_3)_2$), 2.45 (CH_2N), 3.71 (CH_2OCH_2), 4.10 ($POCH_2$), 4.39 (OCH_2CF_3)	C: 40.90% (40.51%) H: 7.45% (6.75%) N: 11.93% (12.88%) Cl: 0.00% (0.17% ppm) F: 9.73% (9.47%)
10b[a]	−7.8	48.0, 59.9, 64.1, 67.5, 69.8, 73.2, 123.6	2.28 ($N(CH_3)_2$), 2.45 (CH_2N), 3.71 (CH_2OCH_2), 4.10 ($POCH_2$), 4.10 (OCH_2CF_3)	C: 34.65% (34.80%) H: 5.80% (6.75%) N: 10.11% (11.58%) Cl: 0.00% (994 ppm) F: 20.87% (21.96%)
10c[a]	−8.0	48.0, 59.9, 64.1, 67.5, 69.8, 73.2, 123.6	2.36 ($N(CH_3)_2$), 2.40 (CH_2N), 3.69 (CH_2OCH_2), 4.05 ($POCH_2$), 4.40 (OCH_2CF_3)	C: 28.20% (27.86%) H: 3.97% (4.73%) N: 8.22% (8.34%) Cl: 0.00% (0.15%) F: 32.15% (33.17%)
11[c]	0.8 (TFE)(NHR)P, −7.6 $(TFE)_2P$	38.5, 44.8, 59.8, 62.8 (m), quartet for CF_3 not observed	2.17 ($N(CH_3)_2$), 2.32 (CH_2NMe_2), 2.97 ($PNCH_2$), 3.72 (PNH), 4.23 (OCH_2CF_3)	C: 27.16% (27.03%) H: 4.27% (4.50%) N: 13.82% (13.82%) Cl: 0.00% (2110 ppm) F: 32.47% (32.45%)
12[c]	−5.3 (PhO)(NHR)P, −17.7 $(PhO)_2P$	38.5, 44.8, 59.4, 121.2, 123.0, 123.6, 128.9, 158.1	1.82 ($N(CH_3)_2$), (CH_2NMe_2) (not observed, may overlap), 2.69 ($PNCH_2$), 3.50 (PNH), 7.20−6.65 (OPh)	C: 57.61% (56.07%) H: 5.84% (5.76%) N: 12.65% (11.65%) Cl: 0.00% (957 ppm)

[a] NMR analysis in CD_3OD. [b] Peaks are broad. The chemical shift corresponds to the center of the peak. [c] NMR analysis in $CDCl_3$, TFE = CF_3CH_2O-, and R = $-CH_2CH_2N(CH_3)_2$.

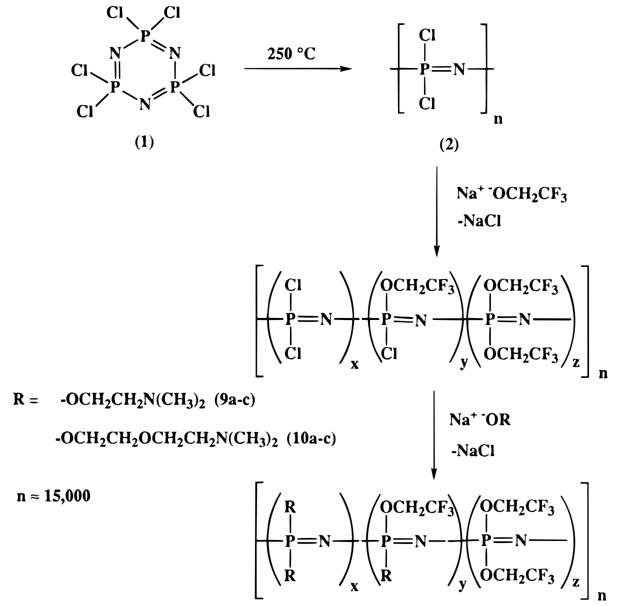
$(CH_3)_2$ proved to be a more effective procedure than the use of $NaOCH_2CH_2N(CH_3)_2$. This was due mainly to the low solubility of the sodium alkoxide in dioxane, which made dilute reaction conditions necessary. Increased dilution requires corresponding increases in reaction time and results in a greater likelihood that complete chlorine replacement may not occur. However, when $HOCH_2CH_2N(CH_3)_2$ was used instead of the sodium salt, complete chlorine replacement took place with minimal backbone cleavage. This was indicated by the presence of a singlet resonance at −8.6 ppm in the ^{31}P NMR spectrum with only minute resonances at −4 and −7 ppm. Thus, substitution proceeds relatively cleanly when the free alcohol is used. It also suggests that the broad NMR peaks detected when the sodium salt was employed result from an interaction between the tertiary amino group and the phosphazene backbone. With the free alcohol, the tertiary amino component acts as an internal hydrogen chloride acceptor, and this reduces the nucleophilic character of the tertiary amine. During purification, the resultant $-CH_2N(CH_3)_2 \cdot HCl$ sites could be deprotonated by rapid treatment with aqueous K_2CO_3 to produce the free tertiary amino groups.

The isolation of **6** as a fully substituted polymer is surprising because the polymer precipitated from solution as the reaction progressed. However, this process produced the highest degree of chlorine replacement (only 135 ppm Cl remaining) based on elemental microanalysis. It is possible that the P−Cl bonds in this system are activated by transient adduct formation between backbone phosphorus atoms and the tertiary amino groups.

It should be noted that tetrahydrofuran (THF) is not an appropriate solvent for these reactions. During the attempted reactions of $[NPCl_2]_n$ with $NaOCH_2CH_2N(CH_3)_2$ in THF, evidence was obtained for the formation of THF oligomers identified by ^{1}H and ^{13}C NMR spectroscopy and by DSC analysis.

Polymers **6** and **7** were off-white or tan materials after purification. Both polymers were soluble in water, methanol, THF, or chloroform. However, they became less soluble after prolonged storage, especially after extended drying under reduced pressure. Reanalysis

Scheme 1. Polymerization and Cosubstitution Pathway



of the polymers after several months' exposure to the atmosphere provided evidence for hydrolysis. This conclusion was based on a decrease in the carbon content (by elemental microanalysis) and the emergence of broad resonances near 0 ppm in the ^{31}P NMR spectrum. The polymers also darkened to an orange-brown color and gave off an amine odor.

Several unsuccessful attempts were made to synthesize fully substituted single-substituent polymers of formula $[NP(NHCH_2CH_2N(CH_3)_2)_2]_n$ by the treatment of $[NPCl_2]_n$ with $NH_2CH_2CH_2N(CH_3)_2$ in 1,4-dioxane or methylene chloride. Partially substituted macromolecules precipitated from solution, and these hydrolyzed during purification. This was indicated by the presence of broad resonances near 0 ppm in the ^{31}P NMR spectrum. The premature precipitation and incomplete substitution is probably due to formation of the tertiary amine hydrochloride. Even when a large excess of triethylamine was employed as an additional hydrochloride acceptor, the tertiary amino groups were apparently sufficiently protonated to bring about polymer precipitation.

Synthesis of Mixed-Substituent Polymers. (a) Polymers with $-OCH_2CH_2N(CH_3)_2$ or $-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ Groups. The difficulties associated with the syntheses of the single-substituent polymers prompted attempts to prepare mixed-substituent alternatives that contained hydrophobic cosubstituent units. Mixed-substituent polymers of formula $[NP(OCH_2CH_2N(CH_3)_2)_x(OCH_2CF_3)_{2-x})]_n$ and $[NP(OCH_2CH_2OCH_2CH_2N(CH_3)_2)_x(OCH_2CF_3)_{2-x})]_n$, where $x \approx 0.5$, 1.0, or 1.5, were synthesized. The ratio of trifluoroethoxy to tertiary amino alkoxy groups was varied in order to alter the balance of hydrophobic to hydrophilic side units. These polymers (**9a**−**c**, **10a**−**c**) were prepared by the sequential treatment of $[NPCl_2]_n$ first with sodium trifluoroethoxide and then with the sodium tertiary amino alkoxide (Scheme 1).

The sequential cosubstitution method allowed the ratio of the substituents to be varied over a range of trifluoroethoxy content from ~25% for **9a** and **10a**, 50% for **9b** and **10b**, to 75% for **9c** and **10c**. Side products were not apparent (based on ^{31}P NMR spectroscopy) when the trifluoroethoxy groups were introduced first. The cosubstituent ratios obtained are listed in Table 3.

Table 3. Polymer Substituent Ratios (9a−c, 10a−c, 11, and 12)[a]

polymer	−OR	−OR′
9a	$-OCH_2CH_2N(CH_3)_2$ (74%)	$-OCH_2CF_3$ (26%)
9b	$-OCH_2CH_2N(CH_3)_2$ (48%)	$-OCH_2CF_3$ (52%)
9c	$-OCH_2CH_2N(CH_3)_2$ (18%)	$-OCH_2CF_3$ (82%)
10a	$-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ (75%)	$-OCH_2CF_3$ (25%)
10b	$-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ (50%)	$-OCH_2CF_3$ (50%)
10c	$-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ (27%)	$-OCH_2CF_3$ (73%)
11	$-NHCH_2CH_2N(CH_3)_2$ (33%)	$-OCH_2CF_3$ (67%)
12	$-NHCH_2CH_2N(CH_3)_2$ (26%)	$-OC_6H_5$ (74%)

[a] The percentages of substituent groups shown are based on analysis of the final purified polymers with the use of a best fit combination of ^1H NMR and elemental microanalysis data.

Multiple ^{31}P NMR resonances (−6.0 to −8.0 ppm) were detected for these mixed-substituent polymers due to the different chemical environments at the phosphorus sites. The presence of both (*N*,*N*-dimethylamino)alkoxy and trifluoroethoxy groups was confirmed by ^1H and ^{13}C NMR spectroscopy, and the ratio of these groups was estimated by integration of the ^1H NMR spectrum and by elemental microanalysis. The mixed-substituent polymers (**9a**−**c**, **10a**−**c**) ranged from off-white to tan in color and were soluble in methanol, THF, and chloroform. Some solubility in water was evident with low loadings of trifluoroethoxy groups (**9a** and **10a**), but most of these mixed-substituent polymers were insoluble in water. This is a reflection of the hydrophobic character of the trifluoroethoxy groups. However, all the mixed-substituent polymers that contained $-OCH_2CH_2N(CH_3)_2$ or $-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ groups decomposed slowly by hydrolysis when exposed to moisture for long periods of time. Increased loadings of the trifluoroethoxy groups slowed the hydrolysis but did not prevent it.

(b) Polymers with $-NHCH_2CH_2N(CH_3)_2$ Groups. As discussed above, synthetic limits exist when attempts are made to replace all the chlorine atoms in $[NPCl_2]_n$ by $NHCH_2CH_2N(CH_3)_2$ groups alone. In view of this, attempts were made to prepare mixed-substituent species of structure $[NP(NHCH_2CH_2N(CH_3)_2)_{0.66}(OCH_2CF_3)_{1.34})]_n$ (**11**) and $[NP(NHCH_2CH_2N(CH_3)_2)_{0.52}(OC_6H_5)_{1.48})]_n$ (**12**). It was anticipated that the high loading of the trifluoroethoxy or phenoxy groups would improve the solubility and help prevent precipitation of the polymer during the reactions. Sequential treatment of **2** with either $NaOCH_2CF_3$ or $NaOC_6H_5$ followed by $NH_2CH_2CH_2N(CH_3)_2$ yielded the respective mixed-substituent polymers. This reaction sequence was used to maintain polymer solubility throughout the substitution and to avoid acid−base interactions between sodium trifluoroethoxide or sodium phenoxide and the amine hydrochloride salts. Tetrahydrofuran could be used as a solvent in these reactions with no detectable signs of solvent oligomerization.

Due to the large differences in phosphorus environments imparted by the alkylamino, trifluoroethoxy, or phenoxy groups, several distinct resonances were detected in the ^{31}P NMR spectra. For example, in the case of $[NP(NHCH_2CH_2N(CH_3)_2)_{0.52}(OC_6H_5)_{1.48})]_n$, the presence of two phenoxy groups on the same phosphorus was indicated by a resonance near −18 ppm. The peak at −5.3 ppm was characteristic of a phenoxy and a $NHCH_2CH_2N(CH_3)_2$ group linked to the same phosphorus. For $[NP(NHCH_2CH_2N(CH_3)_2)_{0.66}(OCH_2CF_3)_{1.34})]_n$, phosphorus atoms with two trifluoroethoxy groups were detected by a peak at −7.6 ppm, while a relatively sharp resonance at 0.8 ppm was attributed to phosphorus atoms linked to one trifluoroethoxy group and one $NHCH_2CH_2N(CH_3)_2$ group. These assignments were made by analogy with the spectra of other mixed-substituent polyphosphazenes containing trifluoroethoxy, phenoxy, and alkylamino groups.[32]

Both **11** and **12** were soluble in THF and chloroform, but they were insoluble in water. The trifluoroethoxy mixed-substituent derivative was a slightly opaque, adhesive elastomer that formed films that adhered well to glass. The phenoxy mixed-substituent derivative was a significantly tougher material that also adhered to glass. Both polymers demonstrated decreased solubility after vacuum-drying, but the polymers remained much more soluble initially if $NH_2CH_2CH_2N(CH_3)_2$ was the only amine employed during the reaction, in other words, when triethylamine was absent. The loss of solubility is possibly due to cross-linking of neighboring chains in the solid state.[33] These polymers appear to be resistant to hydrolysis because no broad resonances were detected in the ^{31}P NMR spectrum, which would indicate the presence of phosphazanes or phosphates. Moreover, the elemental microanalysis remained relatively consistent over time. The polymers retained most of their initial physical characteristics, including an off-white color, after being stored for long periods of time. Additional evidence for hydrolytic stability comes from the model compound studies performed on the cyclic trimer derivatives, which are discussed later. In these studies, the amino linkage to the phosphazene skeleton showed an excellent resistance to hydrolysis.

Thermal Behavior of 6, 7, 9a−c, 10a−c, 11, and 12. The glass transition temperature (T_g) of a polymer is a reflection of the reorientational freedom of a macromolecular chain and the amount of free volume in the solid state. Polyphosphazenes possess an extremely flexible backbone, which results in low T_g's if the side groups are small or flexible.[17a] However, the T_g generally rises as the rigidity and bulkiness of the side groups increase and as hydrogen-bonding becomes possible. For example, The T_g of $[NP(OC_6H_5)_2]_n$ is −8 °C, while that of $[NP(NHC_6H_5)_2]_n$ is 91 °C.[17a] The T_gs for polymers prepared in this study are listed in the Experimental Section. The T_g for polymer **6** was −40 °C, while polymer **7** had a T_g of −50 °C. The glass transition temperatures of the mixed-substituent polymers **9a−c** and **10a−c** are lower than those of their single-substituent tertiary amine counterparts. Similar trends have been found in other mixed-substituent phosphazene polymers with trifluoroethoxy side groups.[34]

The glass transition temperatures for the $-NHCH_2CH_2N(CH_3)_2$ mixed-substituent derivatives **11** and **12** were higher than those of the alkoxy derivatives. The trifluoroethoxy derivative **11** had a T_g of −40 °C. Although this value is near that of **6** and **7**, it is higher than those of mixed-substituent alkoxy derivatives with similar trifluoroethoxy substitution, **10c** ($T_g = -61$ °C) and **9b** ($T_g = -56$ °C). This reflects the opportunities for intra- and intermolecular hydrogen-bonding of −NHR groups in **11**, which reduce polymer chain flexibility. The T_g of the phenoxy mixed-substituent derivative **12** ($T_g = -18$ °C) is considerably higher than that of any of the other polymers. This is probably a result of the combined hydrogen-bonding interactions of the alkylamino groups and the restriction of backbone motion by the bulky, rigid phenoxy substituents.

Hydrolysis Behavior of Model Compounds. In view of the apparent long-term hydrolytic instability of the polymers with $-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ or $-OCH_2CH_2N(CH_3)_2$ side groups, a small molecule study was undertaken to examine the influence of side group structure and pH on the hydrolysis. Cyclic trimers **20** and **21** were chosen because of the known hydrolytic stability of the phenoxy−phosphazene linkages, especially in basic solution.[35] Weakly acidic (pH ∼ 5), nearly neutral (pH ∼ 7−8), weakly basic (pH ∼ 9), and strongly basic (pH ∼ 13) media were utilized. The study was conducted with the compounds dissolved in aqueous diglyme in order to provide a homogeneous system. The progress of hydrolysis was monitored by ^{31}P NMR spectroscopy, and removal of the alkoxy groups was confirmed by a comparison of the ^{31}P NMR spectrum with that of the material produced by Shaw and coworkers through hydrolysis of pentaphenoxy−monochlorocyclotriphosphazene.[36]

Under weakly acidic conditions neither cyclic trimer showed evidence of hydrolysis. However, differences became apparent at pH 7−8. The alkylamino derivative, **21**, showed no evidence of hydrolysis, but the alkoxy derivative, **20**, underwent partial hydrolysis after only 24 h at 22 °C. At 43 °C, **21** still showed no evidence of hydrolysis, even over an 8 day period. During this same time period, more than 80% of the (*N*,*N*-dimethylamino)ethoxy groups of **20** were replaced by hydroxy units at 43 °C. This difference in stability was also detected at pH 9 and 13 although the alkoxy groups were displaced even faster at the higher pH's. These results agree with previous studies in which some alkoxy−phosphazene linkages were found to hydrolyze under basic conditions while alkylamino−phosphazene linkages remained intact.[30,35] This also explains the hydrolytic sensitivity of the (*N*,*N*-dimethylamino)alkoxy polymers (**6**, **7**, **9a−c**, and **10a−c**) in initially neutral aqueous media. The presence of the tertiary amino groups in the polymers and trimers generates basic aqueous solutions through protonation of the amines by water molecules, and this induces the formation of hydroxide ions, which initiate hydrolysis of the oxygen−phosphorus bonds. Even after the polymers are purified and dried, the hygroscopic nature of the tertiary amino groups may accelerate the absorption of atmospheric water and cause subsequent hydrolytic degradation.

Interaction of $(NPCl_2)_3$ and $N_3P_3(OC_6H_5)_5Cl$ with $CH_3CH_2CH_2CH_2N(CH_3)_2$. The detection of several unexpected resonances in the ^{31}P NMR spectrum during reactions of $(NPCl_2)_3$ and $(NPCl_2)_n$ with $NaOCH_2CH_2N(CH_3)_2$ prompted an investigation of the possible formation of coordination compounds between the tertiary amino functionality and the phosphazene backbone. As mentioned previously, several tertiary amines have been reported to react with $(NPCl_2)_3$ to produce materials that range from hydrolytically unstable addition compounds to partly substituted alkylamino phosphazenes. The goal of this section of the investigation was to determine if either of these reactions could occur with the $-OCH_2CH_2N(CH_3)_2$ side groups. The cyclic trimer was used because of the greater ease in the isolation of different reaction products at the small molecule level.

$(NPCl_2)_3$ was treated with *N*,*N*-dimethyl-*n*-butylamine in 1,4-dioxane, and the course of the reaction was monitored by ^{31}P NMR spectroscopy. Evidence for a reaction between $(NPCl_2)_3$ and the tertiary amine was detected after 24 h at 22 °C. The mixture changed from transparent to cloudy, and a doublet (22.3 ppm) and triplet resonance (5.9 ppm) were detected in the ^{31}P NMR spectrum in addition to the singlet (21.4 ppm) from $(NPCl_2)_3$. The doublet and triplet peaks increased in intensity when the reaction was heated to 70 °C, and an additional singlet peak (22.0 ppm) was also detected. These peaks were not the result of hydrolysis, because all the reagents and solvents had been dried exhaustively and strict precautions were taken to exclude moisture.

The reaction products were then converted to their phenoxy derivatives in order to limit hydrolysis during the purification and isolation process. The predominant reaction product was $[NP(OC_6H_5)_2]_3$, but $N_3P_3(OC_6H_5)_5(OH)$ was also detected. However, most significant was the detection of alkylamino derivatives. The major alkylamino-substituted product, with ^{31}P NMR resonances at 32.7 ppm (triplet) and 6.8 ppm (doublet), was found to be $N_3P_3(OC_6H_5)_4(Cl)(N(CH_3)CH_2CH_2CH_2CH_3)$. Alkylamino substitution was confirmed by ^{1}H and ^{13}C NMR spectroscopy. Integration of the ^{1}H NMR spectrum was used to determine the 4:1 ratio of phenoxy to alkylamino groups. Mass spectrometry confirmed the product composition yielding an MH^+ peak at 629 m/z. A small amount of another alkylamino-substituted product was also detected. This material represented by ^{31}P NMR resonances at 30.2 ppm (doublet) and 3.9 ppm (triplet) appears to be $N_3P_3(OC_6H_5)_2(Cl)_2(N(CH_3)CH_2CH_2CH_2CH_3)_2$. This composition was supported by the presence of an MH^+ peak at 564 m/z in the mass spectrum. The remaining chlorine atoms in these structures are probably located on the phosphorus atoms substituted with the alkylamino groups due to the deactivating effect toward P−Cl bond substitution imparted by bulky secondary amines. At the high molecular weight polymer level, the remaining P−Cl sites would hydrolyze over time and lead to the polymer degradation observed in this study.

Additional experiments were conducted with $N_3P_3(OC_6H_5)_5Cl$ in the presence of $CH_3CH_2CH_2CH_2N(CH_3)_2$ to determine the effect of cosubstituent groups on the interaction of a tertiary amine with backbone phosphorus atoms. $N_3P_3(OC_6H_5)_5Cl$ did not react with $CH_3CH_2CH_2CH_2N(CH_3)_2$ even after several days at 70 °C. Thus, it appears that the cosubstituent groups play an important role in the interaction of P−Cl bonds with a tertiary amine. The steric bulk of phenoxy substituents could prevent effective attack of the tertiary amine on the P−Cl bond. Alternatively, cosubstituents could create an electronic environment at the phosphorus atom which discourages the formation of coordination compounds between the tertiary amine and phosphorus atom.

The key conclusion is that both hydrolysis and alkylamino substitution occur when $(NPCl_2)_3$ reacts with $CH_3CH_2CH_2CH_2N(CH_3)_2$. This suggests that the tertiary amine unit in $NaOCH_2CH_2N(CH_3)_2$ can react with phosphorus atoms in $(NPCl_2)_3$ or $(NPCl_2)_n$ to yield side products that are responsible for the unexpected peaks in the ^{31}P NMR spectrum. Furthermore, the formation of highly reactive coordination compounds between the tertiary amino group and the P−Cl units could explain why a fully substituted polymer was obtained when $(NPCl_2)_n$ was treated with $HOCH_2CH_2N(CH_3)_2$.

Conclusions

It is clear that phosphazenes that bear $-OCH_2CH_2N(CH_3)_2$ or $-OCH_2CH_2OCH_2CH_2N(CH_3)_2$ units are sensitive to water even when hydrophobic cosubstituent groups are present. The tertiary amino group may interact with P−Cl bonds to cause side reactions. However, species with $-NHCH_2CH_2N(CH_3)_2$ side groups are stable to neutral and basic media. Synthetic limitations prevent the isolation of single-substituent polymers with this side unit, but mixed-substituent polymers could be prepared. These mixed-substituent polymers appear to offer the best prospects for use as membranes, surface coatings, or ion capture matrixes. Moreover, it appears that the utilization of tertiary amino side groups in polyphosphazenes may be more practical when applied to *surface* functionalization, possibly through displacement of surface trifluoroethoxy side groups. This prospect is currently under investigation.

Experimental Section

Materials. Tetrahydrofuran (EM Science) and 1,4-dioxane (Aldrich) solvents were dried over and distilled from sodium metal using benzophenone as an indicator. Methylene chloride (EM Science) was distilled from calcium hydride. *N*,*N*-dimethylethanolamine, *N*,*N*-dimethylethylenediamine, and 2,2,2-trifluoroethanol (all from Aldrich) were distilled from calcium hydride under an inert argon or nitrogen atmosphere immediately before use. *N*,*N*-dimethylbutylamine (Aldrich) was purified by distillation from potassium hydroxide followed by a series of distillations under nitrogen from sodium/benzophenone, *p*-toluenesulfonyl chloride, and again from sodium/benzophenone. [(*N*,*N*-Dimethylamino)ethoxy]ethanol (TCI of America) was distilled from calcium hydride under reduced pressure. Phenol (Aldrich) was sublimed under vacuum at room temperature. Hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (Ethyl Corp.), was recrystallized from heptane followed by sublimation under vacuum at 40 °C. Poly(dichlorophosphazene) was prepared by the thermal melt polymerization of $N_3P_3Cl_6$ at 250 °C. An average of 35−50% conversion to the high molecular weight polymer was obtained. The remaining cyclic trimer was removed by vacuum sublimation at 40 °C.

Instruments. ^{31}P (144.8 MHz), ^{1}H (360.0 MHz), and ^{13}C (90.0 MHz) NMR spectra were recorded with the use of a Bruker WM360 NMR spectrometer, which employed a broad band CPMAS pencil probe. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P NMR) or tetramethylsilane (^{1}H and ^{13}C NMR). All heteronuclear NMR spectra were proton-decoupled. Differential scanning calorimetry was conducted on a Perkin-Elmer Series 7 system. The T_g's were recorded as the temperature near the midpoint of the transition. Fast atom bombardment mass spectrometry was conducted on a Kratos MS-50 mass spectrometer with a magnetic sector using xenon atoms and a nitrophenyl octyl ether matrix.

Synthesis of $[NP(OCH_2CH_2N(CH_3)_2)_2]_n$ (6). All reactions were performed using standard Schlenk line techniques with dry argon or nitrogen as the atmosphere. Poly(dichlorophosphazene) (1.0 g, 8.9×10^{-3} mol) was dissolved in dry dioxane (250 mL), and the solution was warmed to 45 °C. *N*,*N*-Dimethylethanolamine (7.0 mL, 6.2 g, 7.0×10^{-2} mol) was added by syringe to the polymer solution. After approximately 10 min a white precipitate formed. The reaction mixture was stirred overnight at 45 °C. The mixture was then filtered through a ceramic frit and the polymer dissolved in water (300 mL). Enough potassium carbonate was added to the solution to make it slightly basic (pH ~ 9). The polymer was then immediately dialyzed with deionized water to minimize hydrolysis. The polymer was dialyzed against water for 3 days and against methanol for 3 days with 12 000−14 000 molecular weight cutoff dialysis tubing. The methanol was removed by rotovap and the polymer purified further by precipitation from THF into heptane (done four times). Yield: 1.2 g (61%). T_g: −40 °C.

$[NP(OCH_2CH_2OCH_2CH_2N(CH_3)_2)_2]_n$ (7). [(*N*,*N*-Dimethylamino)ethoxy]ethanol (24.2 g, 0.182 mol) was added by syringe to sodium metal (3.6 g, 0.16 mol) in dry dioxane (400 mL). The mixture was warmed to 50 °C and stirred for 18 h. The resultant sodium salt solution was then transferred via cannula to an addition funnel attached to a reaction flask containing poly(dichlorophosphazene) (3.1 g, 0.027 mol) dissolved in dioxane (400 mL) at 60 °C. The sodium salt was then added dropwise to the warm polymer solution over a period of 8 h. The reaction was allowed to continue for 24 h. The mixture was then concentrated to dryness with a rotary evaporator. The resultant solid was dissolved in deionized water (500 mL) and was dialyzed against water for 4 days and against methanol for 4 days in 12 000−14 000 molecular weight cutoff tubing. The polymer solution was concentrated to dryness and dissolved in THF. Further purification was effected by precipitation of the polymer into heptane (4 times) to give the off-white polymer. Yield: 4.1 (49%). T_g: −50 °C.

$[NP(OCH_2CF_3)_{1.64}(OCH_2CH_2N(CH_3)_2)_{0.36}]_n$ (9c). Because all the mixed-substituent trifluoroethoxy(*N*,*N*-dimethylamino)alkoxy polymer systems were synthesized in a similar manner, the preparation of **9c** is used as a representative example. Poly(dichlorophosphazene) (1.0 g, 8.6×10^{-3} mol) was dissolved in dry dioxane (400 mL). Sodium trifluoroethoxide was prepared by addition of 2,2,2-trifluoroethanol (1.3 g, 1.3×10^{-3} mol) to a mixture of NaH (0.56 g of 60% dispersion in mineral oil, 1.4×10^{-2} mol) in dioxane (100 mL). The sodium trifluoroethoxide solution was then transferred via cannula to an addition funnel and added dropwise to the polymer solution. Meanwhile, sodium (*N*,*N*-dimethylamino)ethoxide was obtained by the addition of the corresponding alcohol (0.40 g, 4.5×10^{-3} mol) to a mixture of NaH (0.18 g, 4.5×10^{-3} mol) in dry dioxane (50 mL). The sodium salt was then transferred to the addition funnel and added dropwise to the partially trifluoroethoxy-substituted polymer. The reaction mixture was stirred for 18 h at 45 °C. The mixture was allowed to cool and then concentrated using a rotary evaporator. The concentrated reaction mixture was dialyzed against water for 3 days and then against methanol for 3 days. Yield: 1.4 g (68%). T_g: polymer **9a** −44 °C, polymer **9b** −56 °C, polymer **9c** −59 °C, polymer **10a** −54 °C, polymer **10b** −59 °C, polymer **10c** −61 °C.

$[NP(OCH_2CF_3)_{1.34}(NHCH_2CH_2N(CH_3)_2)_{0.66}]_n$ (11). Trifluoroethanol (1.2 g, 0.012 mol) was dissolved in THF (20 mL), and the solution was added dropwise to sodium metal (0.3 g, 0.013 mol) in THF (60 mL). The mixture was refluxed for 12 h, allowed to cool to room temperature, and the resultant sodium salt added dropwise to poly(dichlorophosphazene) (1.0 g, 8.6×10^{-3} mol) dissolved in THF (250 mL). The reaction mixture was heated (55−60 °C) for 12 h. This mixture was then added dropwise to a solution of *N*,*N*-dimethylethylenediamine (2.6 g, 0.029 mol) and triethylamine (2.5 g, 0.025 mol) in THF (250 mL) at room temperature. No polymeric precipitate appeared to form. The reaction mixture was stirred for 48 h at room temperature and then warmed for 12 h (55−60 °C). The mixture was allowed to cool to room temperature and was concentrated by rotary evaporator. The concentrated mixture was then precipitated into dilute (1%) aqueous Na_2CO_3. The resultant white material was dried open to the atmosphere overnight, redissolved in acetone, and precipitated again into dilute Na_2CO_3. After an additional 12 h of drying, the polymer was redissolved in THF, concentrated, and precipitated twice more into pentane. The precipitations into pentane resulted in a mobile, white material that solidified to a clear, rubbery solid on evaporation of the pentane. Yield: 0.7 g (29%). T_g: −40 °C.

$[NP(OC_6H_5)_{1.48}(NHCH_2CH_2N(CH_3)_2)_{0.52})]_n$ (12). Phenol (1.6 g, 0.017 mol) was dissolved in THF (50 mL) and added dropwise to sodium metal (0.50 g, 0.022 mol) in THF (50 mL) under nitrogen. The reaction mixture was refluxed overnight to complete the formation of the sodium phenoxide. The phenoxide solution was then transferred to an addition funnel and added dropwise to poly(dichlorophosphazene) (1.3 g, 0.011 mol) in THF (200 mL). The mixture was refluxed for 48 h and then allowed to cool to room temperature. The reaction mixture was filtered and added to *N*,*N*-dimethylethylenediamine (2.3 g, 0.026 mol) in THF (100 mL). The reaction mixture was warmed (55−60 °C) for 2 days and then allowed to cool to room temperature. It was concentrated with a rotary evaporator, and precipitated into dilute (1%) aqueous Na_2CO_3 to afford a white, rubbery material. The material was precipitated from THF into dilute Na_2CO_3 again, then from THF into 95% ethanol, and finally twice from THF into hexanes. The resultant rubbery white product darkened slightly to a tan color when dried under vacuum. Yield: 1.7 g (67%). T_g: −18 °C.

$N_3P_3(OCH_2CF_3)_5Cl$ (13) and $N_3P_3(OC_6H_5)_5Cl$ (14). The syntheses of **13** and **14** were carried out according to reported procedures.[26,37,38]

$N_3P_3(OCH_2CH_2OCH_2CH_2N(CH_3)_2)_6$ (15). [(*N*,*N*-Dimethylamino)ethoxy]ethanol (8.6 g, 0.065 mol) was added to sodium metal (1.6 g, 0.071 mol) stirred in dry THF (400 mL) over a period of 0.5 h. The reaction mixture was then heated to reflux for 12 h in order to form the sodium alkoxide. External heat was removed, and a solution of $(NPCl_2)_3$ (2.5 g, 0.0072 mol) in THF (100 mL) was added to the warm sodium salt solution over 1 h as the flask cooled. The resultant mixture was stirred for 4 h at room temperature. The mixture was filtered to remove salts and unreacted sodium metal. Deionized water (300 mL) was added to the filtered solution, and the resultant solution was washed three times with chloroform (100 mL). The chloroform extracts were combined and washed three times with deionized water (100 mL). The chloroform layer was then dried with $MgSO_4$. The $MgSO_4$ was filtered off and the chloroform removed under reduced pressure. The product was dried under vacuum (0.01 mmHg) at 30 °C for 2 days to yield **15** as a clear yellow oil. Yield: 4.5 g (67%).

$N_3P_3(NHCH_2CH_2N(CH_3)_2)_6$ (17). $(NPCl_2)_3$ (4.0 g, 0.011 mol) was dissolved in dioxane (200 mL) and warmed to 50 °C. Freshly distilled *N*,*N*-dimethylethylenediamine (15.8 g, 0.179 mol) was added to the solution by syringe. A white solid formed almost immediately as the amine was added, but this gradually redissolved to yield a clear, colorless solution. The mixture was warmed overnight at 50 °C and then allowed to cool to room temperature. The solvent was removed under reduced pressure to yield an oily solid. The product was redissolved in THF (150 mL) and extracted twice with 5 M aqueous KOH (200 mL). The THF layer was dried with Na_2SO_4, filtered, and the solvent removed with a rotary evaporator to produce a pale yellow oil. The oil was dried under vacuum to yield a waxy, opaque solid, which became a clear liquid when exposed to moist air. Yield: 0.90 g (12%).

$N_3P_3(OCH_2CF_3)_5(NHCH_2CH_2N(CH_3)_2$ (19). *N*,*N*-dimethylethylenediamine (1.6 g, 0.018 mol) was added to the mixture containing **13** (11.3 g, ~0.006 mol of **13**) in dioxane (200 mL) under argon. The reaction mixture was heated overnight (55−60 °C) and then allowed to cool to room temperature. The solvent was removed under reduced pressure, and the resultant oily material was redissolved in diethyl ether. The ether solution was extracted once with 0.2 M NaOH, dried with K_2CO_3, and filtered. The trimer was further purified by silica gel column chromatography in 75% CH_2Cl_2/25% THF. Removal of the solvent afforded an oily solid. The solid was filtered to yield **19** as a clear, colorless oil. Yield: 0.9 g (~20%).

$N_3P_3(OC_6H_5)_5(OCH_2CH_2N(CH_3)_2$ (20). This trimer was prepared similarly to a method described previously.[26] Specifically, **14** (5.0 g, 0.0079 mol) was dissolved in dioxane (100 mL) under argon. This solution was treated at room temperature with a solution of $NaOCH_2CH_2N(CH_3)_2$, which was prepared through overnight reaction of *N*,*N*-dimethylethanolamine (1.4 g, 0.016 mol) with sodium metal (0.40 g, 0.017 mol) in dioxane (150 mL). The trimer−alkoxide reaction mixture was also stirred at room temperature for 12 h. The solvent was removed under reduced pressure, and the resultant cloudy oil redissolved in Et_2O (200 mL). The ether solution was extracted once with 0.01 M Na_2CO_3 and dried with K_2CO_3. After filtration of the K_2CO_3, the ether was removed under reduced pressure and the resultant oil further purified by silica gel column chromatography in 75% CH_2Cl_2/25% THF. Removal of the solvent afforded a colorless oil that separated from hot hexanes but did not completely crystallize on cooling to −11 °C. The hexanes were decanted, and the material was dried under vacuum to yield **20** as a clear, colorless oil. Yield: 2.3 g (42%).

$N_3P_3(OC_6H_5)_5(NHCH_2CH_2N(CH_3)_2$ (21). *N*,*N*-Dimethylethylenediamine (3.5 g, 0.040 mol) was added by syringe to $N_3P_3(OC_6H_5)_5Cl$ (5.0 g, 0.0079 mol) in THF (250 mL) at room temperature. There was no immediately apparent reaction, so the solution was heated to reflux for 12 h and then allowed to cool to room temperature. The solvent was removed under reduced pressure, and the oily product was redissolved in Et_2O. The ether solution was extracted twice with 0.2 M KOH (100 mL), dried with K_2CO_3, and filtered. The ether was removed under reduced pressure, and the resultant oil was further purified by silica gel chromatography in 75% CH_2Cl_2/25% THF. The solvent was removed under reduced pressure to yield an off-white solid. Attempts to recrystallize the solid from hexanes (100 mL) yielded a cloudy oil. However, the oil solidified to yield **21** as a white powder when dried under vacuum. Yield: 2.2 g (41%).

Hydrolysis of $N_3P_3(OC_6H_5)_5(OCH_2CH_2N(CH_3)_2$ and $N_3P_3(OC_6H_5)_5(NHCH_2CH_2N(CH_3)_2$. The reactions were carried out by dissolving the appropriate trimer (0.3 g) in diglyme (30 mL). The solutions were then converted to the appropriate pH by addition of aqueous buffers or base (pH 5: NaOAc/HOAc (20 mL), pH 7−8 deionized H_2O (20 mL), pH 9: aqueous triethylamine (25 mL), and pH 13: 0.1 M aqueous KOH (20 mL)). The pH level was checked twice a day against pH paper throughout the course of the study, and additional buffer was added when needed. The progress of the hydrolysis was followed by ^{31}P NMR spectroscopy. The reaction mixtures were allowed to stir initially at room temperature for 24 h at 22 °C. The mixtures were then warmed to 43 °C and stirred for 8 days. Reaction samples were taken daily to monitor the extent of hydrolysis and to check the pH.

Reaction of $(NPCl_2)_3$ with $CH_3CH_2CH_2CH_2N(CH_3)_2$. $(NPCl_2)_3$ (5.1 g, 0.015 mol) was dissolved in distilled dioxane (100 mL) under nitrogen. *N*,*N*-Dimethylbutylamine (19.53 g; 0.1930 mol) was added via syringe, and the mixture was stirred at room temperature for 24 h, during which time it became cloudy. The reaction mixture was then heated to 80−90 °C for 72 h. Meanwhile, phenol (16.8 g, 0.178 mol) was dissolved in dioxane (100 mL) under nitrogen. Sodium metal (4.6 g, 0.20 mol) was placed in a separate flask under nitrogen, and dioxane (100 mL) was added to this flask. The phenol solution was then added to the flask containing the sodium via syringe over 30 min. The reaction mixture was then heated to reflux for 12 h to form the phenoxide salt. Next, the phenoxide salt solution was allowed to cool, and the excess sodium was removed. The trimer−amine reaction mixture was then added to the sodium phenoxide solution via syringe, and the reaction mixture was heated to reflux for 24 h. The dioxane was then removed under reduced pressure. The resultant oily salt was partially dissolved in diethyl ether (250 mL) and extracted with deionized water (125 mL). The ether layer was then washed twice with 10% aqueous K_2CO_3 (125 mL) followed by drying with $MgSO_4$. The alkylamino products were isolated by silica gel column chromatography consisting of two columns (70% CH_2Cl_2/30% hexanes). $N_3P_3(OC_6H_5)_4(Cl)(N(CH_3)CH_2CH_2CH_2CH_3)$ was obtained as a white solid through recrystallization from petroleum ether (bp: 40−60 °C). $N_3P_3(OC_6H_5)_2(Cl)_2(N(CH_3)CH_2CH_2CH_2CH_3)_2$ was recovered as an oil through evaporation of the petroleum ether. The products were then dried under vacuum for 48 h.

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