Synthesis and Properties of Poly(aminocarbophosphazenes)

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ABSTRACT: The cyclic carbophosphazene $N_3P_2CCl_5$ undergoes thermal ring-opening polymerization at 120 °C to yield poly(pentachlorocarbophosphazene), $[N_3P_2CCl_5]_n$, as a hydrolytically sensitive elastomer. Treatment of this polymer in solution with primary and secondary alkylamines yielded poly(aminocarbophosphazenes) $[N_3P_2C(NR_1R_2)_5]_n$ where R_1 = H, R_2 = ^{n}Pr or ^{i}Pr, and R_1 = R_2 = Me or Et. These polymers are also sensitive to moisture. An anilino/dimethylamino mixed-substituent polymer, $[N_3P_2C(NHPh)_x(NMe_2)_y(Cl)_z]_n$ (x = 1.50, y = 3.34, z = 0.16), and a 2,6-diphenylphenoxy/dimethylamino mixed-substituent polymer, $[N_3P_2C(2,6\text{-}OPh(Ph)_2)_x(NMe_2)_y]_n$ (x = 1, y = 4), were synthesized via the same technique. A mixed-substituent polymer with regiospecific backbone carbon substitution, $[(NP(OCH_2CF_3)_2)_2NC(N(Ph)_2)]_n$, was also synthesized. These mixed-substituent polymers are stable to water. The macromolecules were characterized by ^{31}P, ^1H, and ^{13}C NMR spectroscopy, IR spectroscopy, elemental analysis, differential scanning calorimetry, thermogravimetric analysis, and gel permeation chromatography. Poly[(dimethylamino)carbophosphazene] undergoes a depolymerization reaction in solution and in the solid state to give small-molecule cyclic analogues, including $N_3P_2C(NMe_2)_5$. The depolymerization reaction was investigated by ^{31}P NMR spectroscopy and thermogravimetric analysis in conjunction with mass spectrometry. Analogous small-molecule model reactions were undertaken in which the cyclocarbophosphazene $N_3P_2CCl_5$ was allowed to react with primary and secondary alkylamines to yield the cyclic species $N_3P_2C(NR_1R_2)_5$. The mixed-substituent cyclic species $\{[NP(OCH_2CF_3)_2]_2[NC(N(Ph)_2)]\}$ and $\{[NP(NMe_2)_2][NP(2,6\text{-}OPh(Ph)_2)(NMe_2)][NC(NMe_2)]\}$ were also synthesized.

Introduction

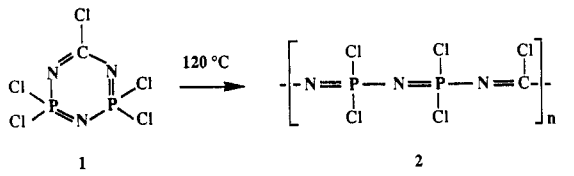
The thermal ring-opening polymerization of inorganic cyclic species is an important route for the preparation of new polymers. The widening interest in novel inorganic macromolecular systems is partly the result of a need for new materials with advanced electrical, optical, thermal, biomedical, or preceramic characteristics.[1]

Recently, we reported the thermal ring-opening polymerization of a cyclocarbophosphazene, $N_3P_2CCl_5$ (**1**), to yield a poly(carbophosphazene), $[N_3P_2CCl_5]_n$ (**2**) (see Scheme 1). Poly(carbophosphazene) **2** was found to undergo facile reactions with aryloxy nucleophiles to give a new class of air- and moisture-stable macromolecules, the poly[(aryloxy)carbophosphazenes]. From a structure/property viewpoint it is of interest that these carbon–phosphorus–nitrogen polymers have higher glass transition temperatures than the correspondingly substituted classical poly[(aryloxy)phosphazenes].[2]

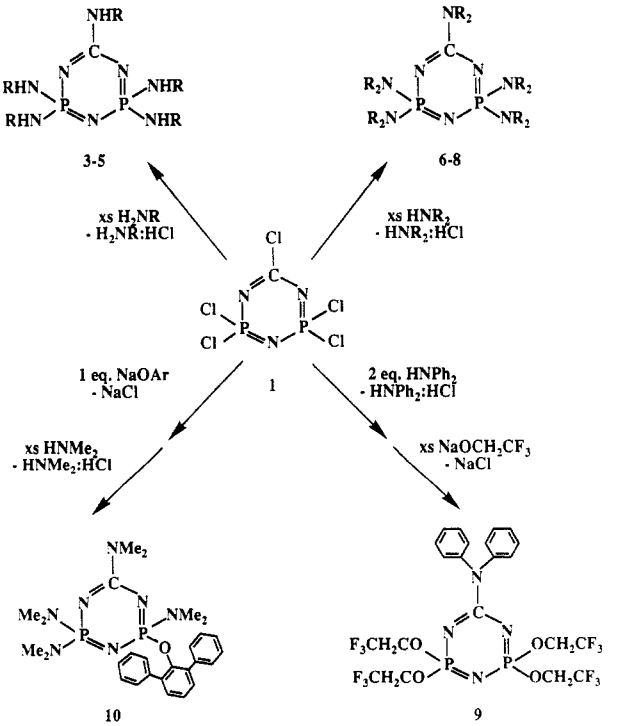
In this paper, we describe the reactions of **1** and **2** with primary and secondary alkylamines such as methylamine, propylamine, isopropylamine, dimethylamine, diethylamine, and piperidine. Compounds **1** and **2** were also treated with diphenylamine and sodium trifluoroethoxide, sodium 2,6-diphenylphenoxide and dimethylamine, and aniline and dimethylamine nucleophiles to give cosubstituent small-molecule cyclic species and polymers (see Schemes 2–4). The properties of the resultant small-molecule cyclocarbophosphazenes **3–10** and the poly(carbophosphazenes) **11–17** are discussed in the following section (see Charts 1 and 2). In particular, the thermal properties of the poly(aminocarbophosphazenes) and the ability of one of these, poly[(dimethylamino)carbophosphazene], to undergo depolymerization at room temperature in solution and in the solid state were investigated.

This is the first reported synthesis of alkylamino derivatives of poly(carbophosphazenes). However, the reactions of amines with small-molecule cyclic carbophosphazenes have been reported previously.[3–6] For example, in 1969 and 1970 Schmidpeter and Schindler published several papers describing the reactions of various amines with cyclocarbophosphazenes of the type $[(NPCl_2)_2$-

Scheme 1



Scheme 2



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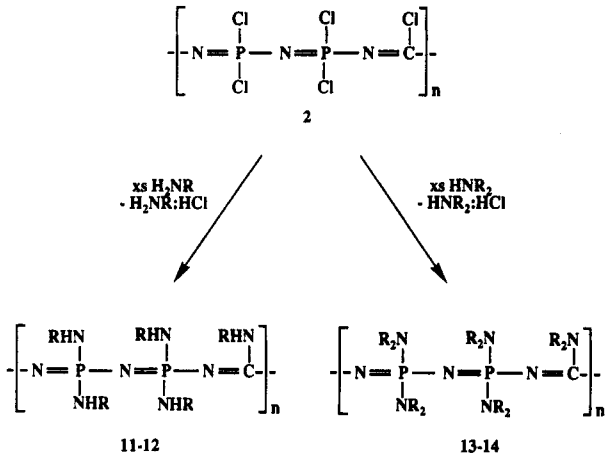
Scheme 3



Scheme 4

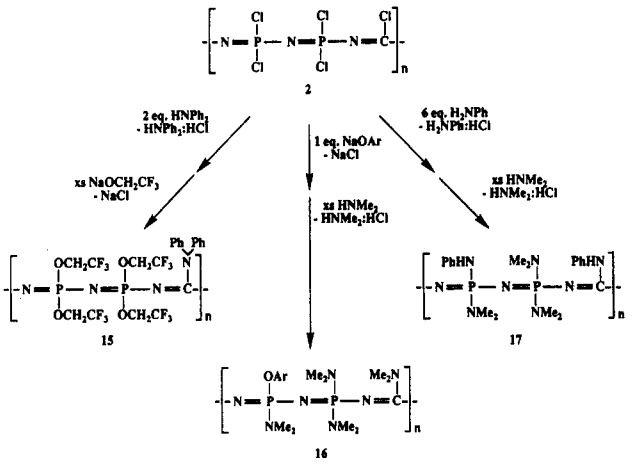
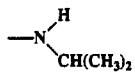
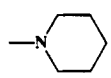
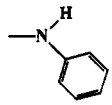


Chart 1

R =	$N_3P_2CR_5$	$[N_3P_2CR_5]_n$
	3[a]	b
	4[a]	11
	5[a]	12
	6	13
	7	14
	8	c
	d	18[d]

[a] These compounds were isolated as mono-HCl adducts. [b] A soluble polymer could not be isolated. [c] The nucleophile degraded the starting polymer 2. [d] This compound has been synthesized previously; see ref 2.

(NCR)], where *R* = an alkyl, aryl, or dimethylamino group.[3-5] These compounds were reported to be crystalline, slightly polar, basic, and generally hydrolytically stable.

Chart 2

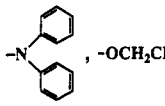
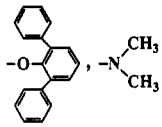
R, R' =	$N_3P_2CR(R')_4$	$[N_3P_2CR(R')_4]_n$
	9	15
	10	16

Table 1. Characterization Data for the Cyclic Aminocarbophosphazenes 3-8

$N_3P_2CR_5$·HCl	^{31}P (ppm)	MS (calcd/found)
3	25.6 (d), 16.0 (d),[a] $^2J_{P-P}$ = 33.2 Hz	302/267[c]
4	22.5 (d), 11.0 (d),[a] $^2J_{P-P}$ = 36.1 Hz	442/407[c]
5	19.7 (d), 8.9 (d),[b] $^2J_{P-P}$ = 37.1 Hz	442/407[c]
$N_3P_2CR_5$	^{31}P (ppm)	MS (calcd/found)
6	32.6[b]	336/336
7	33.2[b]	476/476
8	28.2[b]	536/536

[a] These values were obtained for THF solutions. [b] These values were obtained for toluene solutions. [c] These values were obtained by FAB-MS and correspond to the HCl adduct minus the chloride ion.

To our knowledge, the only other example of the reaction of 1 (containing a carbon–chlorine bond) with an amine was reported by Fluck and Schmid in 1977.[6] They treated 1 with deficiencies of both dimethylamine and diethylamine at low temperature and obtained the corresponding cyclic species $[(NPCl_2)_2(NC(NR_2)]$, where R = Me, Et. They also allowed 1 to react with an excess of both dimethylamine and ethylenimine and obtained the corresponding fully amino-substituted cyclocarbophosphazenes. These compounds were reported to be crystalline. Their hydrolytic stability was not described. As a starting point for the present work, we have repeated the synthesis of one of these compounds, $N_3P_2C(NMe_2)_5$.

Results and Discussion

Synthesis and Properties of Small-Molecule Model Cyclo(aminocarbophosphazenes). The reactions of 1 with a large excess of the primary amines, methylamine, propylamine, and isopropylamine, yielded fully amino-substituted monohydrohalide adducts, $N_3P_2C(NHR)_5$·HCl. The ^{31}P NMR spectra of these adducts contained a pair of doublets with a $^2J_{P-P}$ coupling of approximately 35 Hz. The ^{31}P NMR splitting pattern indicated that one molecule of HCl was coordinated to an amino side group attached to a phosphorus atom. The ^1H NMR spectra showed a broad single resonance in the 8–10 ppm region of the spectrum that can be explained by the formation of amine hydrochloride complexes. The FAB mass spectra showed positive molecular ions consistent with the coordination of one molecule of HCl to compounds 3–5, together with peaks that could be explained by the loss of the associated proton and the sequential loss of amino side groups. These data are summarized in Table 1.

As is the case with some classical cyclotriphosphazenes, the amino-substituted cyclic species are better hydrohalide acceptors than the parent amines.[7] However, unlike the classical cyclotriphosphazene counterparts with the corresponding primary amino substituents, cyclocarbophosphazenes 3–5 are hydrolytically unstable.[7] Therefore, the

Table 2. Characterization Data for the Cyclic Aminocarbophosphazenes 9 and 10

N_3P_2CR/R_4	^{31}P (ppm)	^{13}C (ppm)	^{1}H (ppm)	MS (calcd/found)
9	27.2	165.4 (t) *ring* C, $^{2}J_{C-P}$ = 17.2 Hz, 143.4 *ipso*, 128.7 *meta*, 128.0 para, 126.5 ortho, all singlets, 122.5 (q) OCH_2CF_3, $^{1}J_{C-F}$ = 277.3 Hz, 62.7 (q) OCH_2CF_3, $^{2}J_{C-F}$ = 39.3 Hz	7.3 (m), 4.2 (m)	680/680
10[a]	32.5 (d), 29.3 (d), $^{2}J_{P-P}$ = 39.1 Hz	163.1 (br s) ring C, 149.2 ipso a, 137.3 ipso b, 129.9 meta b, 129.3 meta a, 128.8 ortho a, 127.5 ortho b, 120.9 para a,b, all singlets, 36.1 (d) P-N(CH_3)$_2$, $^{2}J_{C-P}$ = 37.6 Hz, 35.8 (d) P-(N(CH_3)$_2$)$_2$, $^{2}J_{C-P}$ = 31.6 Hz, 35.4 (s) C-N(CH_3)$_2$	7.4 (m), 2.6 (m), 2.4 (d), 2.1 (d)	537/537

[a] The designations a and b in the ^{13}C NMR data for 10 refer to the phenoxy and the phenyl groups of the 2,6-diphenylphenoxy substituent, respectively.

removal of the HCl molecule from 3–5 could not be accomplished by treatment with an aqueous base. In addition, attempts to remove the coordinated HCl by exposure to refluxing triethylamine or pyridine were not successful. Similarly, the HCl could not be removed even when the adduct was treated with condensed ammonia.

The reaction of 1 with a large excess of the secondary amines, dimethylamine, diethylamine, and piperidine, yielded the fully amino-substituted compounds 6–8. These compounds were not obtained as HCl adducts. The ^{31}P NMR shifts of these products in toluene are approximately +30 ppm. Moreover, the ^{1}H NMR spectra contained no peaks that would be characteristic of amine hydrochloride formation. The electron impact mass spectra showed molecular ions, together with peaks assignable to species formed by the sequential loss of amino side groups. These data are summarized in Table 1.

Compound 9 was obtained by the reaction of 1 with 2 equiv of diphenylamine (1 equiv acting as an HCl acceptor) followed by treatment with an excess of sodium trifluoroethoxide. The ^{31}P NMR spectrum showed a singlet resonance at +27.2 ppm, which indicated that the diphenylamine nucleophile had reacted with the carbon–chlorine unit only. The steric bulk of diphenylamine prevents its reaction with classical cyclophosphazenes and polyphosphazenes.[8] Apparently, the carbon atom of 1, which bears only one chlorine substituent versus the two chlorine substituents at the phosphorus atoms, is less hindered. The ^{1}H NMR spectrum showed resonances that were assigned to the aryl protons of the diphenylamino group and the aliphatic protons of the trifluoroethoxy group. The integration of the aryl and aliphatic proton regions indicated a ratio of one diphenylamino group to four trifluoroethoxy groups, as expected for structure 9. The ^{13}C NMR spectrum contained one set of resonances each for the ipso aromatic carbon atom and for the two alkoxy carbon atoms, which indicated that the diphenylamino group reacted with only the C–Cl bond of 1. Previous work has shown that the ipso carbon of an aryloxy group gives rise to two signals (one group attached to carbon and one group attached to phosphorus) in aryloxy-substituted carbophosphazene compounds. A similar feature was observed with the carbon signals of the trifluoroethoxy group.[2] Mass spectrometry showed the correct mass ion at 680. These data are summarized in Table 2.

Compound 10 was obtained by the sequential reaction of 1 with 1 equiv of sodium 2,6-diphenylphenoxide and an excess of condensed dimethylamine. The ^{31}P NMR spectrum contained a pair of doublets centered at +32.5 and +29.3 ppm with a $^{2}J_{P-P}$ coupling of 39.1 Hz. This indicated that the 2,6-diphenylphenoxide nucleophile had reacted with a phosphorus–chlorine bond. Apparently, the steric bulk of 2,6-diphenylphenoxide is not so large that it hinders reaction at the more sterically crowded phosphorus atom. The ^{1}H NMR spectrum contained resonances in the aromatic region of the spectrum which were assigned to the 2,6-diphenylphenoxy group and three resonances at approximately +2.4 ppm which were attributed to the dimethylamino protons (in three different environments). The integration of the aromatic and aliphatic regions of the spectrum indicated approximately one 2,6-diphenylphenoxy group to four dimethylamino groups. The ^{13}C NMR spectrum contained the expected aromatic carbon resonances. One signal was detected for the aromatic ipso carbon. However, three signals were detected for the dimethylamino carbon atom, which corresponded to three different NMR environments (one C–NMe_2 unit, one P–(NMe_2)(OAr) unit, and one P–(NMe_2)$_2$ unit). The signals for the dimethylamino units attached to the phosphorus atoms were split into doublets. The $^{2}J_{P-P}$ coupling was approximately 34 Hz. These data are summarized in Table 2.

Synthesis and Properties of Polymeric Aminocarbophosphazenes. Poly(chlorocarbophosphazene) functions as a reactive macromolecular intermediate. Thus, reactions of 2 with a variety of amine nucleophiles yielded the polymers 11–17. A series of different amine nucleophiles was investigated in order to provide a basis for comparison of the properties of the new polymers with those of their classical polyphosphazene counterparts. The polymers were characterized by ^{31}P NMR, ^{13}C NMR, and ^{1}H NMR spectroscopy, elemental microanalysis, gel permeation chromatography, differential scanning calorimetry, thermogravimetric analysis, and IR spectroscopy. These data are summarized in Tables 3–6.

The reactions of 2 with a large excess of propylamine, isopropylamine, dimethylamine, and diethylamine yielded the fully amino-substituted polymers 11–14 as moisture-sensitive powders that were soluble in polar organic solvents such as THF or chloroform. The ^{31}P NMR spectra of 11–14 contained broad, singlet resonances in the +6.7 to +0.5 ppm region of the spectrum. The ^{1}H and ^{13}C NMR spectra were also consistent with the assigned structures. Thus, low-field resonances ranging from +152 to +171 ppm were assigned to the carbon atoms of the polymer backbone. Although the ^{13}C NMR resonances were generally broad, two different ^{13}C resonances were detected for most of the aliphatic carbon atoms of the amino side groups bound to phosphorus and to carbon atoms in the polymer backbone. The polymer backbone carbon atoms could not be detected in the ^{13}C NMR spectrum of 14. However, the infrared spectra of polymers 11–14 contained intense absorptions at 1400–1480 cm^{-1}. These absorptions were also detected for the previously synthesized poly[(aryloxy)carbophosphazenes] and were assigned to backbone C=N vibrations.[2,9] In addition, characteristic P=N skeletal absorptions were detected at 1250–1300 cm^{-1}.[10]

Elemental microanalyses of 11–14 were consistent with the assigned structures. They showed that small amounts of unreacted residual chlorine or amine hydrochloride salts were present. Residual amine hydrochloride salts were expected because 11–14 could not be purified in the presence of water. The weight-average molecular weight (M_w) of polymers 11–14 was estimated to be in the range

Table 3. NMR Data for the Poly(aminocarbophosphazenes) 11–17

polymer	^{31}P (ppm)	^{13}C (ppm)	^{1}H (ppm)
11	6.7 (br s)	151.6 (t) backbone C, $^{2}J_{C-P}$ = 31.5 Hz; 43.0 (br s) N-CH_2; 25.0 (br s) -$CH2$-; 11.6 (br s) -CH_3	3.2 (br s) NH, 2.8 (br s) -NCH_2-, 1.5 (br s) -CH_2-, 0.9 (br s) -CH_3
12	6.3 (m)	155.6 (t) backbone C, $^{2}J_{C-P}$ = 9.2 Hz; 43.3 (br s) NCH-; 25.5 (br s) -$CH(CH_3)_2$	3.5 (m) NH, 3.3 (br s) -CH, 1.1 (m) -CH_3
13	0.5 (br s)	156.0 (br s) backbone C; 39.7 (s) C-$N(CH_3)_2$; 37.4 (s) P-$N(CH_3)_2$	2.9 (br s) C-$N(CH_3)_2$, 2.6 (br s) P-$N(CH_3)_2$
14	5.4 (br s), -13.6 (br s)	backbone C not detected; 42.8 (s) C-NCH_2-; 39.6 (br s) P-NCH_2-; 13.4 (br s) -CH_3	3.1 (br s) -CH_2-, 1.0 (br s) -CH_3
15	-10.1 (br s)	171.3 (br s) backbone C; 144.4 (s) ipso; 130.0 (s) meta; 127.9 (s) ortho; 126.8 (s) para; 122.9 (q) -CF_3, $^{1}J_{C-F}$ = 277.1 Hz; 63.0 (m) -CH_2-	7.2 (m) aromatic, 4.4 (m) -CH_2-
16[a]	-10.1 (br s)	backbone C not detected; 143.9 (br s) ipso a, ipso b not detected; 129.3 (br s) meta a, 129.0 (br s) meta b; 128.0 (br s) ortho b, 126.9 (br s) ortho a; 121.5 (br s) para a, b, 36.9 (m) -CH_3	7.3 (br s) aromatic, 2.2 (br s) -$PNCH_3$, 2.6 (br s) C-NCH_3
17	13.2 (br s), 4.9 (br s), -7.4 (br s)	165.4 (br s) backbone C; 141.6 (br s) ipso, 129.1 (br s) meta; 121.4 (m) para; 118.2 (m) ortho, 37.3 (br s) P-$N(CH_3)_2$; 34.9 (s) C-$N(CH_3)_2$	7.1 (br s) aromatic, 3.0 (br s) NH, 2.7 (br s) -NCH_3

[a] The designations a and b in the ^{13}C NMR data for **16** refer to the phenoxy and phenyl groups, respectively.

Table 4. Characterization Data for the Poly(aminocarbophosphazenes) 11–17

polymer	GPC	elem anal. (calcd/found)		% yield
11	$M_w = 4.4 \times 10^4$, $M_n = 1.9 \times 10^4$	47.28/45.38	C	38.1
		9.92/9.16	H	
		27.52/25.33	N	
		0.00/2.08	Cl	
12	$M_w = 3.5 \times 10^4$, $M_n = 1.6 \times 10^4$	47.28/45.56	C	71.4
		9.92/9.37	H	
		27.52/24.40	N	
		0.00/1.20	Cl	
13	$M_w = 1 \times 10^4$, $M_n = 2 \times 10^3$	39.28/36.25	C	41.1
		8.99/8.35	H	
		33.31/29.77	N	
		0.00/1.72	Cl	
14	$M_w = 1 \times 10^4$, $M_n = 1 \times 10^3$	52.92/49.52	C	45.8
		10.57/9.35	H	
		23.51/24.88	N	
		0.00/1.82	Cl	
15	$M_w = 3.3 \times 10^4$, $M_n = 1.6 \times 10^4$	36.34/34.22	C	34.3
		2.71/2.61	H	
		6.16/7.14	N	
		0.00/0.25	Cl	
16	$M_w = 7.7 \times 10^3$, $M_n = 1.2 \times 10^3$	65.88/64.88	C	11.1
		6.35/4.38	H	
		14.27/12.26	N	
		0.00/1.87	Cl	
17	$M_w = 5 \times 10^3$, $M_n = 1 \times 10^3$	49.02/46.78	C	28.6
		6.64/7.11	H	
		24.86/30.74	N	
		0.00/1.76	Cl	

Table 5. T_g Data for the Poly(carbophosphazenes) 2 and 11–18

polymer	T_g (°C)	polymer	T_g (°C)
2	-21[a]	15	*b*
11	74	16	*b*
12	78	17	90
13	28	18	112[a]
14	*b*		

[a] See ref 2. [b] The T_g of this polymer could not be detected.

of 1×10^4 by gel permeation chromatography (GPC). These values are, in some cases, an order of magnitude lower than those obtained for the poly[(aryloxy)carbophosphazenes] (approximately 1×10^5).[2] Thus, the strongly basic amine nucleophiles may cause some cleavage of the poly(carbophosphazene) backbone. In addition, **14** had a large polydispersity (10). This may be further evidence that polymer backbone cleavage occurs in the presence of amine nucleophiles.

Table 6. Thermogravimetric Analysis Data for the Poly(aminocarbophosphazenes) 11–18

polymer	peak (°C)	ceramic yield (% at 900 °C)	polymer	peak (°C)	ceramic yield (% at 900 °C)
11	333	36	15	307	8
12	292	30	16	345	36
13	292	7	17	433	30
14	288	25	18	263	40

The hydrolytic instability (assessed by precipitation into distilled water) of **11–14** resulted in rapid molecular weight decline and decomposition of the polymers. This was surprising since the classical (alkylamino)polyphosphazene derivatives are synthesized and/or purified in the presence of water.[10] Furthermore, the previously synthesized poly(anilinocarbophosphazene) **18** is stable toward water.[2b] Thus, an attempt was made to synthesize the cosubstituted poly(carbophosphazenes) **15–17** using bulky nuclephiles in an attempt to sterically shield the backbone carbon site (the presumed site of instability). Indeed, these cosubstituted polymers were found to be hydrolytically stable materials.

The small-molecule model synthesis of **9** indicated that diphenylamine would react only at the carbon site of **2**. Therefore, polymer **15** was synthesized by the reaction of **2** with 2 equiv of diphenylamine. The remaining chlorine atoms were then replaced by reaction with sodium trifluoroethoxide. Polymer **15** was purified by repeated precipitations into both distilled water and hexane and was obtained as a white, moisture-stable powder, that was soluble in common organic solvents.

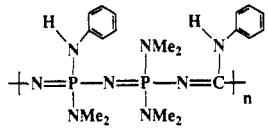
The ^{31}P NMR spectrum of **15** contained a single, broad resonance at -10.1 ppm, and this is consistent with the presence of only one phosphorus environment. The ^{1}H NMR and ^{13}C NMR spectra were also consistent with the assigned structure. The ^{1}H NMR spectrum contained two resonances; a multiplet at +7.2 ppm which was assigned to the diphenylamino protons and a multiplet at +4.4 ppm which was attributed to the aliphatic trifluoroethoxy protons. The lack of a second, smaller resonance in the aliphatic region of the spectrum indicated that the trifluoroethoxy units are attached to only the phosphorus atoms of the polymer backbone. The ^{13}C NMR spectrum contained the expected backbone, aromatic, and aliphatic carbon resonances. Again, only one set of resonances was detected for the ipso aromatic carbon and the aliphatic carbons, and this provided additional proof that site-

specific substitution by the diphenylamino unit had occurred.

The small-molecule model synthesis of **10** indicated that reaction of **2** with 1 equiv of sodium 2,6-diphenylphenoxide was more likely to result in substitution at a phosphorus–chlorine bond than at a carbon–chlorine bond. However, **16** was synthesized with the anticipation that a large, bulky unit anywhere along the macromolecular backbone might shield the backbone carbon sites and, thus, provide some degree of hydrolytic stability. Polymer **2** was treated with 1 equiv of sodium 2,6-diphenylphenoxide. The remaining phosphorus–chlorine and carbon–chlorine bonds were allowed to react with an excess of condensed dimethylamine. Polymer **16** was purified by repeated precipitations into distilled water and hexane and was obtained as a tan, moisture-stable powder, that was soluble in common organic solvents.

The ^{31}P NMR spectrum of **16** contained a broad resonance centered at −10.1 ppm with a shoulder at −1.2 ppm, consistent with a polymer structure containing phosphorus–aryloxy and phosphorus–dimethylamino units. The ^{1}H NMR spectrum of **16** consisted of three resonances at +7.3, +2.6, and +2.2 ppm, corresponding to the 2,6-diphenylphenoxy protons, the carbon-bound dimethylamino protons, and the phosphorus-bound dimethylamino protons. The ^{13}C NMR spectrum of **16** was more difficult to interpret due to the broad signals which were obtained. The aromatic resonances were consistent with the assigned structure, except for the ipso carbon atom of the phenyl rings, which could not be detected. A resonance for the backbone carbon atom was not detected. In addition, only one signal, a multiplet at +36.9 ppm, was detected for the dimethylamino unit. Because there are three different NMR environments for this group, three signals were expected (as seen, for example, in the ^{1}H NMR spectrum of **16**). The broadness of all of the NMR signals may have contributed to the failure to detect three distinct signals. The NMR spectra of polyphosphazenes generally have broader NMR signals than those of the corresponding small molecules. This is partly a consequence of the broad molecular weight distribution of the polymers. In the case of **16**, the polydispersity was approximately 6, which indicated a fairly broad range of molecular weights.

A third mixed-substituent polymer, **17**, which contained



17

anilino and dimethylamino units was also synthesized. Aniline was chosen as one of the cosubstituents because **18**, the previously synthesized, fully anilino-substituted poly(carbophosphazene), is a moisture-stable material. Polymer **2** was first treated with a deficiency of aniline (relative to the chlorine present) and was the further reacted with condensed dimethylamine. A substitution ratio of 60% anilino to 40% dimethylamino units was the target structure (one anilino group attached to every phosphorus or carbon atom along the polymer backbone). However, a polymer was obtained with 30.0% anilino, 66.8% dimethylamino, and 3.2% unreacted chloro units, as determined by ^{1}H NMR integration and elemental microanalysis. The polymer was purified by repeated precipitations into dry hexane. Exposure of **17** to distilled water resulted in no measurable hydrolytic decomposition as deduced by ^{1}H NMR spectroscopy.

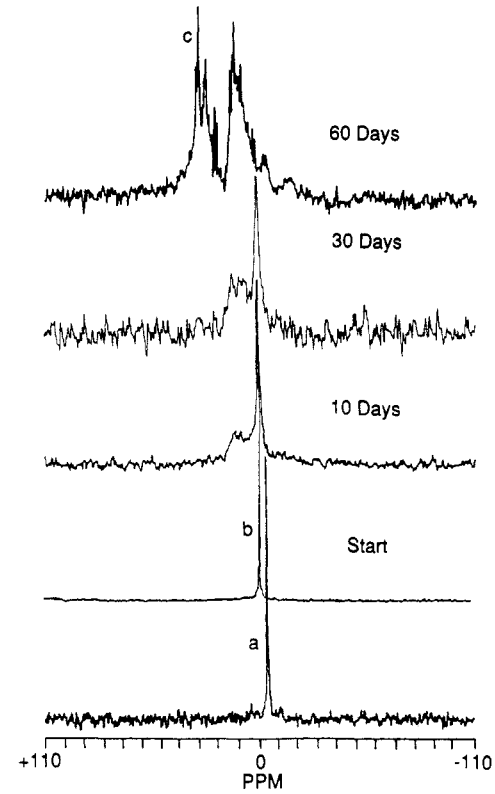


Figure 1. ^{31}P NMR spectra of $[N_3P_2CCl_5]_n$ **2** (a) and $[N_3P_2C(NMe_2)_5]_n$ **13** (b). The spectra at 10, 30, and 60 days show the loss of the signal for **13** and the appearance of a signal for $N_3P_2C(NMe_2)_5$ **6** (c).

The ^{31}P NMR spectrum of **17** contained three broad, overlapping resonances at +13.2, +4.9, and −7.4 ppm. These resonances were assigned to P–$(NMe_2)_2$ units, P–(NMe_2)(NHPh) units, and P–$(NHPh)_2$ units, respectively. The ^{1}H NMR spectrum showed three broad, singlet resonances at +7.1, +3.0, and +2.7 ppm, which corresponded to the aromatic anilino protons, the amino proton, and the dimethylamino protons, respectively. The integration of the aromatic vs the aliphatic region of the spectrum suggested a substitution ratio of approximately 30% anilino groups to 70% dimethylamino groups. Elemental microanalysis of **17** indicated that 3.2% unsubstituted chloro units remained. Analysis of the found percentages of carbon and hydrogen suggested an anilino substitution in **17** of 30.0% and a dimethylamino substitution of 66.8%. The ^{13}C NMR spectrum contained the expected backbone, aromatic, and aliphatic carbon resonances. Two signals at +37.3 and +34.9 ppm were assigned to the dimethylamino–phosphorus unit and the dimethylamino–carbon unit, respectively.

The infrared spectra of polymers **15–17** contained intense absorptions at 1400–1480 cm^{-1}. These were assigned to backbone C=N vibrations.[2,9] Characteristic P=N vibrations were also detected at 1250–1300 cm^{-1}.[10] Elemental microanalyses of **15–17** were consistent with the assigned structures. Small amounts of unreacted chlorine were detected in all cases. The M_w of polymers **15–17** was estimated to be in the range of 5×10^3–8×10^4 by GPC. As in the weight-average molecular weights determined for **11–14**, these values are 1–2 orders of magnitude lower than those determined for previously synthesized poly(carbophosphazenes).[2]

Thermal Transition Behavior of the Poly(aminocarbophosphazenes) 11–18. 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. Classical polyphosphazenes possess an extremely flexible polymer backbone. When the side groups are small and nonbulky, very low T_g's are observed. For example, the T_g of $[NPCl_2]_n$ is −63 °C.[10] However, as the rigidity and bulkiness of the side groups increase, a higher T_g is generated. For example, the T_g of $[NP(NMe_2)_2]_n$ is −4 °C, the T_g of $[NP(NC_5H_{10})_2]_n$ is 19 °C, and the T_g of $[NP(NHPh)_2]_n$ is 91 °C.[10]

The poly(carbophosphazenes) possess an inherently less flexible macromolecular chain than do classical polyphosphazenes. For example, the T_g of $[N_3P_2CCl_5]_n$ **2** is −21 °C, approximately 40 °C higher than that of $[NPCl_2]_n$.[2] This decreased skeletal flexibility of poly(carbophosphazenes) is thought to be a consequence of the high barrier to torsional mobility of C=N bonds ($p\pi$–$p\pi$) vs P=N bonds ($d\pi$–$p\pi$). Thus, the C=N bonds act as stiffening units in the macromolecular backbone.[2]

The T_g values for the poly(aminocarbophosphazenes) **2** and **11**–**18** are shown in Table 5. These glass transition temperatures follow the general trend of increasing T_g with an increase in the rigidity and bulkiness of the side group. For example, the T_g's increase in the order **2** (R = Cl) −21 °C < **13** (R = NMe_2) 28 °C < **11** (R = NH^nPr) 74 °C ≅ **12** (R = NH^iPr) 78 °C < **17** (R = 30.0% NHPh, 66.8% NMe_2) 90 °C < **18** (R = NHPh) 112 °C. This trend can be explained by the increase in intramolecular steric interactions between side groups and by the lower free volume of the system when side groups with these characteristics are present. Comparison of the T_g's of the correspondingly substituted classical aminophosphazene polymers with the T_g's of **13** and **18** shows that the glass transition temperatures of **13** and **18** are 24 and 21 °C higher, respectively, than those of $[NP(NMe_2)_2]_n$ and $[NP(NHPh)_2]_n$. Thus, the poly(aminocarbophosphazenes) possess less backbone torsional mobility than their classical poly(aminophosphazene) counterparts.

Depolymerization of Poly[(dimethylamino)carbophosphazene] (13). The polymerization and depolymerization of classical phosphazenes are believed to be different aspects of a common ring–polymer equilibration process. In general, small, sterically undemanding side groups favor the polymerization process, while bulkier groups favor depolymerization. We have suggested that some poly(organophosphazenes) are actually thermodynamically unstable materials at room temperature but are useable at moderate temperatures because of an extremely slow *rate* of depolymerization.[10] The dimethylamino unit is a fairly small substituent that would not be expected to favor depolymerization. Indeed, classical poly[(dimethylamino)phosphazene] undergoes cross-linking reactions at elevated temperatures (100–500 °C) to produce a matrix material rather than depolymerization to small-molecule cyclic compounds.[11] Therefore, it is surprising that poly[(dimethylamino)carbophosphazene] (**13**) is thermally unstable at room temperature in both the solid and solution states.

Polymer **13** was prepared from pure **2** (containing no cyclic monomer **1**) and was purified by filtration and repeated precipitation into dry hexane under an inert atmosphere. The polymer, which was initially a white powder, liquified to an oil after storage in the solid state for several days under argon at room temperature. Figure 1 shows the ^{31}P NMR spectrum of the purified polymer **2**, which was further treated with condensed dimethylamine to yield **13**. The ^{31}P NMR signal of a sample of **13** dissolved in dry toluene, which was initially a clean singlet at +0.5 ppm, became broader and developed a shoulder

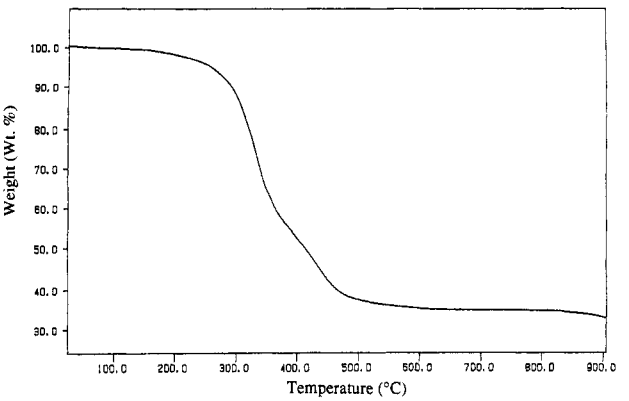


Figure 2. Thermogravimetric analysis curve for $[N_3P_2C(NH^nPr)_5]_n$ **11**. A heating rate of 20 °C/min was employed.

at +10 ppm after 10 days. This shoulder became more pronounced after 30 days. The ^{31}P NMR spectrum after 60 days showed that very little of **13** remained. Instead, multiple signals centered at +10 and +25 ppm were observed. One of these, a singlet at +32.6 ppm, corresponded to the ^{31}P NMR shift found for the small-molecule cyclic $N_3P_2C(NMe_2)_5$ (compound **6**) (see Figure 1).

The presence of **6** in the mixture of products suggested that **13** depolymerizes at room temperature to give various dimethylamino-substituted small molecules. Electron impact mass spectrometry of the products obtained after 60 days confirmed this. The following cyclic phosphazenes and carbophosphazenes were detected: $N_5P_4C(NMe_2)_9$ (mass = 602), $N_4P_3C(NMe_2)_7$ (mass = 469), $N_4P_4(NMe_2)_8$ (mass = 444), $N_3P_3(NMe_2)_6$ (mass = 399), and $N_3P_2C(NMe_2)_5$ (mass = 336). The same ^{31}P NMR spectra were obtained from a sample of **13** stored under argon in dry toluene at room temperature, albeit over a much longer time period. The depolymerization of **13** was substantially slower when stored under argon at −55 °C. At this temperature the polymer was stable for several months.

Thermal Behavior of Poly(aminocarbophosphazenes). In general, organic polymers are sensitive to heat and will decompose with the loss of their useful polymeric properties when subjected to temperatures in excess of a few hundred degrees. On the other hand, polymers that possess inorganic backbones usually have a greater resistance to heat. The polyphosphazenes are one such class of inorganic polymers.[12]

The thermal stability and behavior of classical polyphosphazenes depend to a large degree on the nature of the side groups. Three types of behavior may occur at high temperature: (1) random chain cleavage of the phosphazene macromolecule, (2) depolymerization to form small-molecule cyclic species, or (3) cross-linking reactions that result in the formation of ultrastructures. Classical poly(aminophosphazenes) undergo loss of amines above 100–150 °C with subsequent cross-linking. The yield of the resultant ultrastructure (ceramic) at 1000 °C is 20–30%.[13]

In this section the thermal behavior of the amino-substituted poly(carbophosphazenes) **11**–**18** is discussed. The polymers were analyzed at 50–900 °C by thermogravimetric analysis (TGA) techniques used in conjunction with electron impact mass spectrometry. The temperature at which the greatest weight loss was detected and the final ceramic yield at 900 °C of **11**–**18** are shown in Table 6. A representative thermogravimetric analysis curve is shown in Figure 2.

Polymers **11**, **12**, **14**, and **16**–**18** all showed significant weight loss occurring between 175 and 500 °C. Mass

spectrometry indicated that the volatile products detected between 175 and 500 °C consisted overwhemingly of the corresponding free amine and, in the case of 11, 12, and 14, of propane and butane. Very small amounts of cyclocarbophosphazenes were also detected throughout this temperature range. Polymer 13 underwent an onset of weight loss at a lower temperature (100 °C). At 500 °C, 13 had lost over 90% of its weight. Mass spectrometry indicated that the volatile products detected between 100 and 500 °C consisted mainly of dimethylamine and the cyclic carbophosphazene 6. This is consistent with the ^{31}P NMR data of 13 at room temperature, which indicated the depolymerization of 13 to 6. Polymer 15 showed an onset of weight loss at 175 °C. At 450 °C 15 had lost approximately 90% of its weight. Mass spectrometry indicated that the volatile products detected between 175 and 500 °C consisted of the small-molecule cyclic phosphazenes $N_3P_3(OCH_2CF_3)_6$ and $N_4P_4(OCH_2CF_3)_8$. Small amounts of diphenylamine were also detected.

The ceramic yields of the poly(aminocarbophosphazenes), with the exception of 13 and 15, were fairly high, ranging from 25 to 40% at 900 °C, indicating that ultrastructure materials were formed. The high ceramic yield and the loss of free amines and small-molecule organic species between 175 and 500 °C indicated that the poly(aminocarbophosphazenes) 11, 12, and 14, 16–18 follow the last of the three breakdown patterns described above: specifically the loss of side groups resulting in cross-linking reactions and ultrastructure formation.

Polymers 13 and 15 both had low ceramic yields (7% and 8%, respectively). The small amount of residue remaining at 900 °C from 13 is consistent with the proposed thermal depolymerization of the polymer to cyclic species. Polymer 15, which contained approximately 80% trifluoroethoxy units and only about 20% of the diphenylamino group, probably depolymerizes rather than undergoing cross-linking reactions. Classical polyphosphazenes which contain trifluoroethoxy units are known to depolymerize at temperatures between 200 and 400 °C.[13] Thus, polymers 13 and 15 follow the second thermolysis pathway described above: depolymerization to form small-molecule species which then volatilize.

Experimental Section

Equipment and Materials. The cyclocarbophosphazene 1 was synthesized by a modification of the method of Fluck et al.[14] A two-step route was employed as described below using phosphorus pentachloride, ammonium chloride, and cyanamide, which were obtained from Aldrich. Cyanamide was recrystallized from diethyl ether before use and was stored under argon at −55 °C. 1,1,2,2-Tetrachloroethane and nitrobenzene were dried over molecular sieves (Davison 4 Å). Compound 1 was sublimed twice before use and was stored in a drybox (Vacuum Atmospheres). Tetrahydrofuran, dioxane, and diethyl ether (Aldrich) were distilled from sodium benzophenone ketyl. Toluene, hexane, and methylene chloride (Aldrich) were distilled from calcium hydride. Methylamine was obtained from Linde, and dimethylamine was obtained from Matheson. All other amines and alcohols were obtained from Aldrich. Liquid amines were distilled from barium oxide before use. Gaseous amines were passed through drying tubes containing barium oxide or potassium hydroxide. All reactions and manipulations were carried out under an inert atmosphere using either a drybox or standard Schlenk techniques and with the use of dried, distilled solvents.

^{31}P (^1H-decoupled) NMR spectra were obtained with a JEOL FX-90Q NMR spectrometer operated at 36.2 MHz and with a Bruker WP-360 NMR spectrometer operated at 146 MHz. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as external reference, with positive shift values downfield from the reference. ^1H NMR and ^{13}C NMR spectra were recorded with the use of a Bruker WP-360 spectrometer operated at 360 and 90 MHz, respectively. Chemical shifts are relative to external TMS. Infrared spectra were obtained with the use of a Perkin-Elmer 283B grating spectrometer. Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. The molecular weights of the polymers were estimated by gel permeation chromatography (GPC) with the use of a Hewlett-Packard HP 1090 liquid chromatograph equipped with a refractive index detector. Two Phenomenex Phenogel columns ($0–10^7$ mixed bed) were calibrated with narrow molecular weight polystyrene standards. A 0.1% n-Bu_4NBr solution in THF was used as the eluent. DSC and TGA analyses were recorded with the use of a Perkin-Elmer Series 7 thermal analysis system equipped with a PE 7500 computer. Electron impact mass spectra were obtained with use of a AEI MS 950 instrument.

Syntheses. $N_3P_2CCl_5$ (1). Step 1. $[Cl_3PNPCl_3]^+Cl^-$ was synthesized in three steps following the procedure of Becke-Goehring and Lehr (^{31}P = +19.6 ppm in methylene chloride, yield 50%).[15]

Step 2. $[Cl_3PNPCl_3]^+Cl^-$ (15.0 g, 46.3 mmol) was suspended in hexane (200 mL), and the suspension was cooled to 0 °C. Cyanamide (2.02 g, 48.1 mmol) was dissolved in diethyl ether (100 mL) and was added to the stirred suspension dropwise, under argon. The reaction mixture was allowed to warm to room temperature overnight. The mixture was gently warmed at 35–40 °C for 1 day. The diethyl ether was removed under vacuum, and the hexane liquors were transferred via cannula to a Schlenck flask. Hexane (100 mL) and diethyl ether (100 mL) were added to the unreacted residue, and the reaction was allowed to proceed for an additional 1 day at 35–40 °C. At this time, only a small amount of unreacted material remained. Again the diethyl ether was removed under vacuum, and the hexane liquors were transferred via cannula to the Schlenk flask. The hexane was removed under vacuum, and the resulting solid was transferred to a sublimator and was vacuum sublimed twice (50–100 μm) using an oil bath at 40–55 °C (yield 7.8 g, 57%; ^{31}P = +36.2 ppm in THF).

$[N_3P_2CCl_5]_n$ (2). Compound 1 (2.0 g, 6.8 mmol) was sealed in a heavy-walled glass tube under high vacuum (50 μm). The tube was placed in an oven fitted with a rocker shelf and was heated at 120 °C. After 3–5 h a clear, viscous melt was obtained. The tube was removed from the oven and opened in a glovebag under an argon atmosphere. The tube contents were dissolved in dioxane. A concentrated solution was precipitated into hexane (200 mL) in order to remove unpolymerized 1. The hexane was decanted from pure 2, which was dried under vacuum. The purified polymer 2 was used immediately (yield 1.5 g, 75%; ^{31}P = −4.2 ppm in toluene).

$N_3P_2C(NHMe)_5{\cdot}HCl$ (3). Compound 1 (0.50 g, 1.70 mmol) was dissolved in toluene (50 mL). Gaseous methylamine was passed through barium oxide and condensed into the cooled reaction flask (0 °C) at −78 °C for 15 min. A white precipitate formed. The reaction solution was filtered, and the toluene was removed under vacuum. The resultant material was redissolved in methylene chloride and recrystallized from a methylene chloride/hexane mixture. Yield 0.46 g, 90.2%.

The synthesis of 6 followed the procedure described above for 3. Gaseous dimethylamine was passed through drying tubes containing potassium hydroxide. Yield 0.49 g, 86.0%.

$N_3P_2C(NH^nPr)_5{\cdot}HCl$ (4). A solution of propylamine (3.0 g, 51.0 mmol) in toluene (10 mL) was added dropwise to a solution of 1 (0.50 g, 1.70 mmol) in toluene (50 mL). A white precipitate formed. The solution was warmed for 2 h (60 °C). The solution was filtered to remove amine hydrochloride, and the toluene was removed under vacuum. The crude material was redissolved in methylene chloride and recrystallized from a methylene chloride/hexane mixture. Yield 0.53 g, 70.7%.

The synthesis of 5, 7, and 8 followed the procedure described above for 4. The following yields were obtained: 5, 0.45 g, 60.0%; 7, 0.64 g, 79.0%; 8, 0.77 g, 84.6%.

$N_3P_2C(NPh_2)(OCH_2CF_3)_4$ (9). A solution of diphenylamine (0.59 g, 3.50 mmol) in toluene (10 mL) was added dropwise to a solution of 1 (0.50 g, 1.70 mmol) in toluene (50 mL). The reaction mixture was refluxed overnight. The solution was cooled. A white precipitate appeared; the reaction mixture was filtered through an airless filter funnel. The toluene was removed under vacuum and replaced with THF (30 mL). A solution of sodium

trifluoroethoxide, prepared from trifluoroethanol (1.36 g, 13.6 mmol) and sodium (0.32 g, 14.0 mmol) in THF (30 mL), was added dropwise to the reaction flask. The mixture was refluxed overnight. Compound **9** was purified by column chromatography on silica with a methylene chloride/hexane mixture as the eluent. Yield 0.55 g, 47.6%.

$N_3P_2C(2,6\text{-}Ph_2C_6H_3O)(NMe_2)_4$ (10). A solution of sodium 2,6-diphenylphenoxide, prepared from 2,6-diphenylphenol (0.43 g, 1.75 mmol) and sodium (0.04 g, 1.80 mmol) in dioxane (30 mL), was added to a cooled solution (0 °C) of **1** (0.50 g, 1.70 mmol) in dioxane (30 mL). The reaction mixture was warmed to room temperature overnight. The mixture was again cooled to 0 °C, and gaseous dimethylamine was passed through potassium hydroxide and then condensed into the reaction flask at −78 °C for 15 min. The reaction solution was filtered. The dioxane was removed under vacuum. Crude **10** was extracted with toluene, and the toluene solution was concentrated under vacuum. Compound **10** was purified by recrystallization from methylene chloride/hexane. Yield 0.43 g, 47.3%.

$[N_3P_2C(NH^nPr)_5]_n$ (11). A solution of **2** (1.5 g, 5.1 mmol) in toluene (250 mL) was added slowly, dropwise, to a solution of *n*-propylamine (15.3 g, 0.26 mol) in toluene (50 mL). Formation of a precipitate was noted immediately upon addition of the polymer solution to the amine solution. The reaction solution was stirred at room temperature for approximately 18 h. The reaction solution was gravity filtered in an airless filter flask under argon. The filtered solution was concentrated under vacuum until a viscous solution was obtained. The viscous polymer solution was precipitated into hexane (three times) under an atmosphere of argon. Polymer **11** was further purified by dialysis against THF (molecular weight cutoff = 1000). The polymer was retrieved from the dialysis liquors and dried under vacuum. A pale yellow, powdery material was obtained.

The synthesis of polymers **12** and **14** followed the procedure described above for **11**. Polymer **12** was purified by precipitation into hexane (three times). Polymer **14** was purified by precipitation into hexane (three times) and by dialysis in THF (molecular weight cutoff = 1000).

$[N_3P_2C(NMe_2)_5]_n$ (13). Gaseous dimethylamine was passed through potassium hydroxide and condensed at −78 °C into a solution of **2** (1.5 g, 5.1 mmol) in toluene (250 mL) at 0 °C. Formation of a white precipitate was noted immediately. The addition of dimethylamine continued for 1–2 h. The cold reaction solution was transferred to an airless filter funnel and was gravity filtered. The resultant solution was concentrated under vacuum until a viscous solution was obtained. The viscous polymer solution was precipitated into cold hexane (three times). Polymer **13** was dried under vacuum and was obtained as a white, flaky powder. The polymer was stored under argon at −55 °C.

$[N_3P_2C(NPh_2)(OCH_2CF_3)_4]_n$ (15). A solution of diphenylamine (2.3 g, 13.6 mmol) in toluene (50 mL) was added dropwise to a solution of **2** (1.5 g, 5.1 mmol) in toluene (200 mL). The reaction mixture was refluxed overnight and allowed to cool. A precipitate formed from the cooled solution. The solution was filtered through an airless filter funnel. The toluene was removed under vacuum and was replaced with THF (200 mL). A solution of sodium trifluoroethoxide, prepared from trifluoroethanol (5.4 g, 54.4 mmol) and sodium (1.3 g, 56.5 mmol) in THF (100 mL), was added to the polymeric intermediate via cannula. The reaction mixture was refluxed overnight. The solution was filtered and concentrated under vacuum. The concentrated polymer solution was precipitated into hexane (twice) and distilled water (twice) and was dried under vacuum. A white powder was obtained.

$[N_3P_2C(2,6\text{-}Ph_2C_6H_3O)(NMe_2)_4]$ (16). A solution of sodium 2,6-diphenylphenoxide, prepared from 2,6-diphenylphenol (1.68 g, 6.82 mmol) and sodium (0.17 g, 7.5 mmol) in dioxane (50 mL), was added dropwise to a cooled solution (0 °C) of **2** (1.5 g, 5.1 mmol) in dioxane (150 mL). The solution was warmed at approximately 60 °C for 2 days and then cooled to 0 °C. Gaseous dimethylamine was passed through potassium hydroxide and condensed into the reaction flask at −78 °C for 1–2 h. The reaction solution was filtered, and the dioxane was removed under vacuum. A concentrated THF solution of **16** was precipitated into hexane (twice) and distilled water (twice). Polymer **16** was further purified by dialysis in THF/methanol (molecular weight cutoff = 1000). The polymer was dried under vacuum and was obtained as a pale yellow powder.

$[N_3P_2C(NHPh)_{1.50}(NMe_2)_{3.34}(Cl)_{0.16}]_n$ (17). A solution of aniline (2.8 g, 30.6 mmol) in toluene (50 mL) was added dropwise to a solution of **2** (1.5 g, 5.1 mmol) in toluene (150 mL). The reaction mixture was warmed gently (~50 °C) for several hours. A precipitate formed in the solution. The reaction flask was cooled to 0 °C, and gaseous dimethylamine was passed through potassium hydroxide and condensed into the reaction mixture at −78 °C. The reaction solution was filtered in an airless filter funnel. The filtered solution was concentrated under vacuum and precipitated into hexane (three times). Polymer **17** was dried under vacuum and obtained as a white powder.

Thermogravimetric Analysis of the Poly(aminocarbophosphazenes) 11–18. The polymer samples (2–5 mg) were analyzed under a constant flow of nitrogen in platinum pans at a heating rate of 20 °C/min with an initial temperature of 50 °C and a final temperature of 900 °C. The instrument was calibrated by using the magnetic standards alumel (163 °C), nickel (354 °C), and peralloy (596 °C). Mass spectral data were obtained with the use of a KRATOS MS9/50 magnetic sector instrument via the direct insertion probe (DIP) method. Samples were ionized via electron impact at 70 eV.

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Author Supplied Registry Numbers. 1, 57332-66-8; 2, 132492-02-5; PCl_5, 10026-13-8; NH_4Cl, 12125-02-9; H_2NCN, 420-04-2; $[Cl_3PNPCl_3]^+Cl^-$, 57646-88-5; 2,2,2-trifluoroethanol, 75-89-8; methylamine, 74-89-5; dimethylamine, 124-40-3; propylamine, 107-10-8; isopropylamine, 75-31-0; diethylamine, 109-89-7; piperidine, 110-89-4; diphenylamine, 122-39-4; 2,6-diphenylphenol, 2432-11-3; aniline, 62-53-3.