Organosiloxyphosphazene Polymers: Synthesis via Aminosiloxane Reagents[1]

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ABSTRACT: Cyclic and high polymeric phosphazenes have been synthesized with aminosiloxane side groups either as the sole substituent or with cosubstituents such as OCH_2CF_3, $OCH_2CH_2OCH_2CH_2OCH_3$, or OC_6H_5. Small-molecule model compound reactions were first carried out between $N_3P_3(OPh)_5Cl$ and $H_2N(CH_2)_3SiMe_2OSiMe_3$ or $H_2N(CH_2)_3Si(OSiMe_3)_3$ to yield the pentaphenoxymonoaminosiloxy derivatives $N_3P_3(OPh)_5NH(CH_2)_3SiMe_2OSiMe_3$ and $N_3P_3(OPh)_5NH(CH_2)_3Si(OSiMe_3)_3$. Following the structural identification of these species, similar reactions were carried out between the high polymeric phosphazenes $[NP(R)_xCl_y]_n$, where R = OCH_2CF_3, OPh, or $OCH_2CH_2OCH_2CH_2OCH_3$, $x = 0, 0.5$, or 1.5, $y = 2 - x$, and $n = 15\,000$, and the same two aminosiloxanes. The molecular structures of the final polymers were deduced from a combination of elemental analysis and ^1H NMR integration. The substituent distribution and thermal-, surface-, and solid-state properties of the aminosiloxyphosphazene polymers are described.

The synthesis of new polymers with a phosphazene backbone and organosilicon side groups offers the prospect of access to new materials with unusual characteristics.[2-8] Such polymers may combine the advantages of polysiloxanes[9] with those of polyphosphazenes.[10] Their behavior as membranes, elastomers, and biomaterials is of considerable interest.

In earlier papers we described synthetic routes to such polymers (a) by the phosphazene ring-opening polymerization of cyclic trimeric silyl- and siloxy-[4] cyclophosphazenes and (b) via the reactions of lithiophenoxyphosphazenes with chlorosilanes and cyclotrisiloxanes.[8] Method (a) has the advantage that it allows the synthesis of polyphosphazenes that bear organosilicon side groups attached to the polymer via Si–C–P linkages, but it suffers from the disadvantage that only a limited variety of organosilyl side groups can survive the conditions needed for ring-opening polymerization of the cyclotriphosphazene. (Organosilyl)lithium reagents cannot be used for reactions with high polymeric chlorophosphazenes because of their tendency to cleave the backbone bonds.[11] Method (b) uses an organometallic macromolecular substitution process for the linkage of organosilicon units to an aryloxyphosphazene polymer. This method imposes certain restrictions on the range of polymer structures accessible. For example, the method is at present restricted to aryloxyphosphazenes (which are soluble in a limited range of solvents). Moreover, no more than 80% of the aryloxy side groups can be used as sites for organosilicon unit linkage.

Our objective in this present work was to bypass the disadvantages of methods (a) and (b) by the use of a side group that avoids organometallic chemistry. Thus, we describe here reactions of *amino*siloxanes with poly(dichlorophosphazene) and poly(organochlorophosphazenes). By this process, it was possible to design and synthesize poly(organophosphazenes) with a well-defined ratio of oligo or polysiloxane side groups. As in our previous studies, the reactions were first investigated at the small molecule model compound level before being transposed to the analogous macromolecules.

Results and Discussion

Small-Molecule Model Compound Studies. It is well-known that chlorophosphazene cyclic oligomers and high polymers react with primary or secondary amines to yield aminophosphazenes. However, it is also known that such reactions are sensitive to steric retardation if the incoming amine, or the organic groups already present, are bulky units.[12,13] Our purpose in this work was to explore the use of two aminosiloxy nucleophiles, $H_2N(CH_2)_3SiMe_2OSiMe_3$ and $H_2N(CH_2)_3Si(OSiMe_3)_3$, both of which could be sensitive to steric hindrance effects. Thus, an initial objective of this research was to examine the behavior of these two reagents when allowed to react with the hindered cyclophosphazene $N_3P_3(OPh)_5Cl$ (1).

Species 1 was prepared as described previously.[8] The aminosiloxane (3-aminopropyl)pentamethyldisiloxane was synthesized via the well-known hydrosilylation reaction between (*N*-trimethylsilyl)allylamine and pentamethyldisiloxane.[14] The reaction shown in Scheme I took place under relatively mild conditions in THF at 66 °C to give species 2 and 3 in 60% and 35% isolated yields, respectively.

The structural proof for these compounds is given in Table I. The conversion of 1 to 2 was quantitative as determined by ^{31}P NMR spectroscopy. However, the reaction between $H_2N(CH_2)_3Si(OSiMe_3)_3$ and 1 to yield **3** was slower than the similar reaction that produced 2 (residual starting material was still present after 10 h at 66 °C). Although the branched aminosiloxane was subject to some steric retardation, replacement of the shielded chlorine atom by both amino nucleophiles was possible. Thus, the prospects for the analogous macromolecular reactions seemed promising.

High Polymer Substitution Reactions. (A) Single Substituent Reactions. Four different types of reactions were investigated, as illustrated in Scheme II. First, an attempt was made to replace all the chlorine atoms in poly(dichlorophosphazene) (4) by $H_2N(CH_2)_3SiMe_2OSiMe_3$ to give polymer 5. Complete replacement of the halogen atoms occurred even under mild reaction condi-

Scheme I

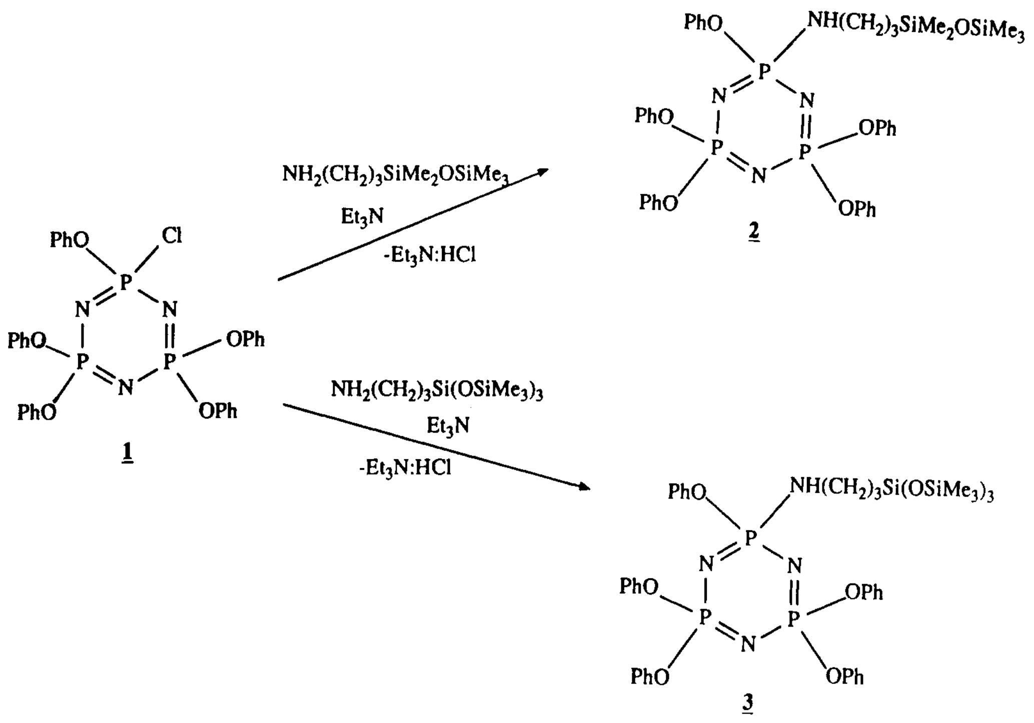


Table I
Analytical Data for $H_2N(CH_2)_3SiMe_2OSiMe_3$ and $N_3P_3(OPh)_5R$

compound	mass spectral data calcd	mass spectral data found	signal	^{1}H NMR[a]	elemental anal.	elemental anal. calcd	elemental anal. found
$H_2N(CH_2)_3SiMe_2OSiMe_3$ (2a)	205	206[b]	H_2N[c]	1.1 (s, 2 H)	C	46.75	46.71
			H_2NCH_2	2.5 (t, 2 H)	H	11.30	11.18
			$H_2NCH_2CH_2$	1.3 (m, 2 H)			
			$H_2NCH_2CH_2CH_2$	0.4 (m, 2 H)			
			$SiMe_2OSiMe_3$	0.1 (s, 15 H)			
$N_3P_3(OPh)_5(NH(CH_2)_3SiMe_2OSiMe_3)$ (2)	804	804[d]	HN	1.6 (s, 1 H)	C	56.70	56.75
			$HNCH_2$	2.5 (t, 2 H)			
			$HNCH_2CH_2$	1.3 (m, 2 H)	H	5.90	6.42
			$HNCH_2CH_2CH_2$	0.2 (m, 2 H)			
			$SiMe_2OSiMe_3$	0.0 (s, 15 H)	N	6.96	6.83
			OPh	7.1 (m, 25 H)			
$N_3P_3(OPh)_5(NH(CH_2)_3Si(OSiMe_3)_3)$ (3)	952	952[d]	HN	1.6 (s, 1 H)			
			$HNCH_2$	2.5 (t, 2 H)	C	52.92	52.97
			$HNCH_2CH_2$	1.4 (m, 2 H)			
			$HNCH_2CH_2CH_2$	0.3 (m, 2 H)	H	6.24	6.30
			$Si(OSiMe_3)_3$	0.1 (s, 27 H)			
			OPh	7.2 (m, 25 H)	N	5.88	5.66

[a] Proton NMR reported in ppm relative to external TMS (0 ppm) in $CDCl_3$. [b] Mass found was M + 1 because of the chemical ionization method. No parent peak was found when electron impact was used. [c] Amine protons were exchangeable with D_2O. [d] In addition to the parent peak, fragments resulting from loss of OPh, $SiMe_3$, methyl, and $OSiMe_2$ were identified.

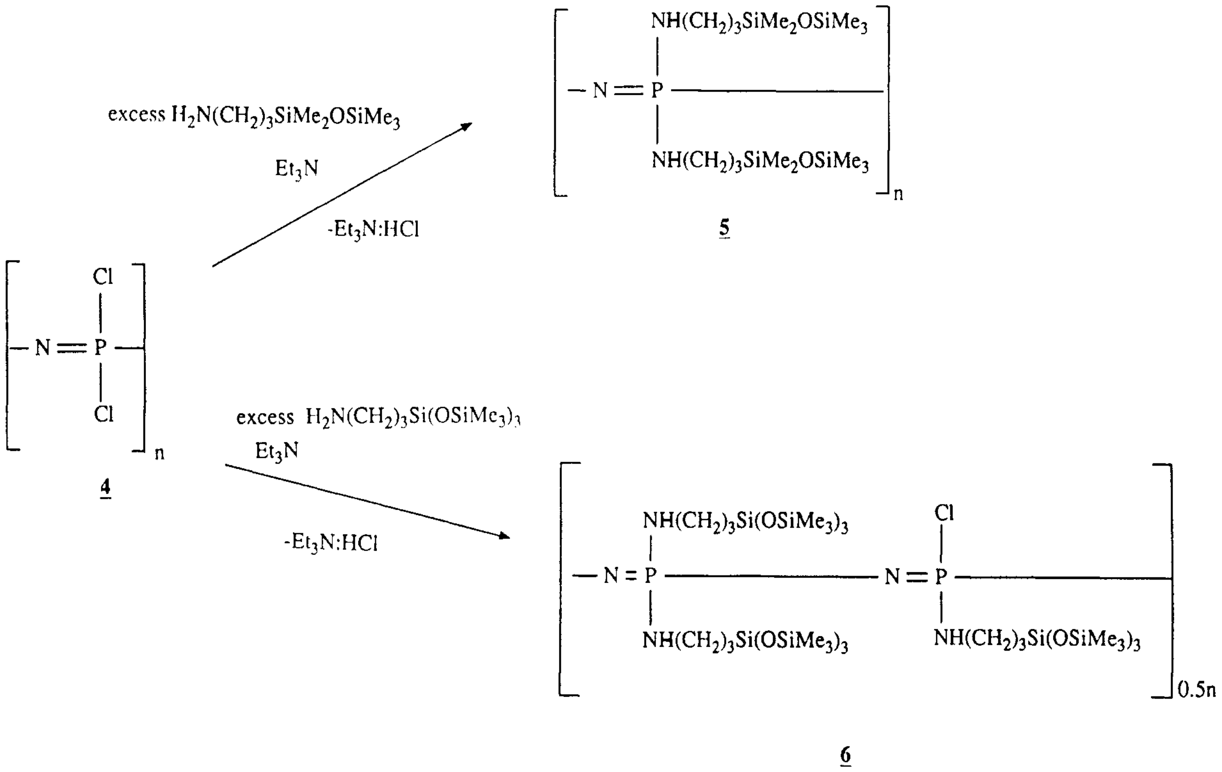
tions (see Experimental Section). Polymer 5 after purification was a stable material with a glass transition temperature (T_g) of −67 °C. Thermal and surface contact angle measurements are listed in Tables II and III and are discussed later.

Attempts to carry out a similar reaction with the use of $H_2N(CH_2)_3Si(OSiMe_3)_3$ as a nucleophile resulted in the replacement of only 80–90% of the chlorine atoms in 4 by the aminosiloxy unit. This behavior is attributed to steric hindrance effects. The remaining chlorine atoms were so shielded that they proved to be stable to water even during many months of exposure to the atmosphere.

The difference in the reactivity of $H_2N(CH_2)_3SiMe_2OSiMe_3$ and $H_2N(CH_2)_3Si(OSiMe_3)_3$ toward $[NPCl_2]_n$ (4) was monitored by following the changes in the ^{31}P NMR spectra. As shown in Figure 1, the ^{31}P NMR spectrum of 5 is a relatively sharp singlet centered around +3.5 ppm, a value that is similar to the chemical shift of poly[bis(*n*-propylamino)phosphazene] ($\delta = 4.1$ ppm). However, the ^{31}P NMR spectrum of 6 is a broad singlet with a chemical shift centered at −1.5 ppm. The broadness of the signal and its upfield chemical shift is the result of different phosphorus atom environments generated by incomplete substitution. Elemental microanalysis data, together with ^{31}P NMR data, support the conclusion that 6 contained residual chlorine atoms under these reaction conditions. Attempts to induce a reaction of the remaining P–Cl bonds by using higher boiling solvents such as dioxane or excess $H_2N(CH_2)_3Si(OSiMe_3)_3$ failed to bring about replacement of all the chlorine.

The possibility was then explored that the aminosiloxanes could be introduced as cosubstituents in reactions with polyphosphazenes that bore trifluoroethoxy, (meth-

Scheme II



oxyethoxy)ethoxy, or phenoxy side groups as well as chlorine units. This approach allowed the ratio of the organosilicon side group to the organic side group to be varied over a wide range, with the final ratio being controlled by the degree of substitution by the first nucleophile. The three organic substituents were selected because they covered a range from hydrophobic unhindered units (OCH_2CF_3), through hydrophilic, relatively unhindered groups ($OCH_2CH_2OCH_2CH_2OCH_3$), to hydrophobic hindered units (OPh) (see Scheme III).

(B) Mixed-Substituent Polymers Containing the Trifluoroethoxy Unit. Poly[bis(trifluoroethoxy)phosphazene], $[NP(OCH_2CF_3)_2]_n$, is a microcrystalline material with a T_g of -66 °C and a T_m of 240 °C. The trifluoroethoxy group is a powerful electron-withdrawing substituent, which would be expected to sensitize the nearby P–Cl bonds to nucleophilic attack. Indeed, this reaction was used in the mid-1960s to produce the first hydrolytically stable polyphosphazene.[15]

Thus, 4 was allowed to react with a stoichiometric deficiency of sodium trifluoroethoxide. The resultant (trifluoroethoxy)chloropolyphosphazene was then treated with excess aminosiloxane in the presence of triethylamine as a hydrohalide acceptor. Four structural combinations were explored on the basis of the formation of two different reactive intermediates. Thus, $[NP(OCH_2CF_3)_{0.5}Cl_{1.5}]_n$ (7) and $[NP(OCH_2CF_3)_{1.5}Cl_{0.5}]_n$ (8) were allowed to react with $H_2N(CH_2)_3SiMe_2OSiMe_3$ or $H_2N(CH_2)_3Si(OSiMe_3)_3$. The products (9–12) are depicted in Scheme III. No difficulty was experienced with the introduction of the second side group, even when the branched aminosiloxane side unit was employed.

The structural characterization of polymers 9–12 was accomplished by a combination of ^1H NMR and elemental analysis. The results are shown in Tables II and III. The ^{31}P NMR spectra for polymers 9 and 10, which have approximately 75% of side groups as aminosiloxane units, contained a broad singlet centered at -1.0 ppm and a smaller signal at -8.0 ppm, with a relative intensity of approximately 6:1. These resonances correspond to $N\mathit{P}(NHR)_2$, $N\mathit{P}(NHR)(OCH_2CF_3)$, and a small amount of $\mathit{P}(OCH_2CF_3)_2$, respectively.[16] In polymers 11 and 12, the ^{31}P NMR signals were at -8.0 and -1.0 ppm. These correspond to the presence of $N\mathit{P}(OCH_2CF_3)_2$ and $N\mathit{P}(OCH_2CF_3)(NHR)$ units. The origins of these signals will be considered later.

Those derivatives with the lower concentration of aminosiloxy units (9 and 10) were elastomers. The polymers that possessed ~75% of side groups as aminosiloxy units (11 and 12) were rigid, amorphous materials.

(C) Mixed-Substituent Polymers Containing the (Methoxyethoxy)ethoxy Group (15–18). The (methoxyethoxy)ethoxy side group ($OCH_2CH_2OCH_2CH_2OCH_3$) imparts an unusual set of properties to polyphosphazenes. When it is the only side group present, it generates a low T_g (-84 °C), water solubility, and sensitivity to cross-linking by γ-irradiation. An unusual degree of molecular mobility in the solid state, coupled with the ability to dissolve salts such as $LiCF_3SO_3$, has generated interest in its use as a solid electrolyte.[17] It was therefore of some interest to study its behavior as a cosubstituent with the hydrophobic aminosiloxane units.

The four polymers 15–18 were synthesized via polymeric intermediates 13 and 14 in a manner similar to that described for the trifluoroethoxy cosubstituent polymers. The elemental analysis data were consistent with products in which virtually complete replacement of the chlorine atoms in 13 and 14 by the unbranched amine $H_2N(CH_2)_3SiMe_2OSiMe_3$ had occurred. However, species 16 contained a high percentage of unreacted chlorine (an amount that corresponds to approximately one chlorine in seven repeat units). This incomplete substitution is probably a consequence of steric hindrance by the branched amine $H_2N(CH_2)_3Si(OSiMe_3)_3$. The composition and characterization data for the final polymers are listed in Tables II and III.

Table II
Analytical Data for Mixed-Substituent Polymers[a]

					elemental anal.	
compound	$M_n \times 10^{-4}$	$M_w \times 10^{-5}$	T_g, °C		calcd	found
$[NP(NH(CH_2)_3SiMe_2OSiMe_3)_2]_n$ (**5**)	5.1	5.9	−67	C	42.33	41.14
				H	9.79	8.75
				N	9.26	9.57
				Cl	0.00	1.05
$[NP(NH(CH_2)_3Si(OSiMe_3)_3)_{1.8}Cl_{0.2}]_n$ (**6**)	6.0	6.0	−128[b]	C	36.98	36.26
			−88 (T_c)	H	8.79	8.25
			−55 (T_m)	N	5.84	3.72
				Cl	1.62	1.41
$[NP(OCH_2CF_3)_{0.5}(NH(CH_2)_3SiMe_2OSiMe_3)_{1.5}]_n$ (**9**)	14.7	21.2	−57	C	38.91	39.45
				H	8.56	9.01
				N	8.73	9.03
				Cl	0.00	0.11
$[NP(OCH_2CF_3)_{0.6}(NH(CH_2)_3Si(OSiMe_3)_3)_{1.35}]_n$ (**10**)	13.0	10.0	−45	C	35.88	36.32
			−130[b]	H	8.15	7.84
				N	5.65	5.85
				Cl	0.30	0.67
$[NP(OCH_2CF_3)_{1.45}(NH(CH_2)_3SiMe_2OSiMe_3)_{0.48}]_n$ (**11**)	4.3	14.2	−70	C	28.16	28.67
				H	4.53	5.00
				N	7.21	6.52
				Cl	0.25	0.18
$[NP(OCH_2CF_3)_{1.5}(NH(CH_2)_3Si(OSiMe_3)_3)_{0.5}]_n$ (**12**)	17.0	39.0	−36	C	29.22	29.67
			−129[b]	H	5.45	5.65
				N	5.68	5.24
				Cl	0.00	0.04
$[NP(MEE)_{0.6}(NH(CH_2)_3SiMe_2OSiMe_3)_{1.33}]_n$ (**15**) (MEE = $OCH_2CH_2OCH_2CH_2OCH_3$)	10.4	19.5	−75	C	41.91	41.59
				H	9.25	8.67
				N	8.35	8.39
				Cl	0.63	0.42
$[NP(MEE)_{0.5}(NH(CH_2)_3Si(OSiMe_3)_3)_{1.35}$	5.3	4.6	−88	C	38.04	38.68
			−129[b]	H	8.23	7.49
				N	5.66	4.99
				Cl	1.19	1.29
$[NP(MEE)_{1.4}(NH(CH_2)_3SiMe_2OSiMe_3)_{0.55}]_n$ (**17**)	10.1	38.5	−78	C	42.00	41.58
				H	8.50	8.68
				N	6.67	6.48
				Cl	0.54	0.27
$[NP(MEE)_{1.5}(NH(CH_2)_3Si(OSiMe_3)_3)_{0.5}]_n$ (**18**)	5.9	5.5	−77	C	40.53	38.77
			−128[b]	H	8.44	7.67
				N	5.25	4.33
				Cl	0.00	0.17
$[NP(OPh)_{0.4}(NH(CH_2)_3SiMe_2OSiMe_3)_{1.55}]_n$ (**21**)	10.4	19.5	−59	C	44.34	44.73
				H	9.08	9.07
				N	8.91	9.30
				Cl	0.44	0.21
$[NP(OPh)_{0.55}(NH(CH_2)_3Si(OSiMe_3)_3)_{1.25}]_n$ (**22**)	8.0	12.0	−11	C	40.38	39.96
			−127[b]	H	8.38	7.62
				N	5.79	5.56
				Cl	1.30	1.57
$[NP(OPh)_{1.4}(NH(CH_2)_3SiMe_2OSiMe_3)_{0.6}]_n$ (**23**)	12.0	11.0	−30	C	53.20	52.56
				H	6.83	6.75
				N	7.52	7.53
				Cl	0.00	0.06
$[NP(OPh)_{1.5}(NH(CH_2)_3Si(OSiMe_3)_3)_{0.5}]_n$ (**24**)	16.0	26.0	−11	C	49.89	49.71
				H	6.85	7.29
				N	5.82	5.65
				Cl	0.00	0.03

[a] When the sum of substituents per phosphorus is less then 2, then mass balance is made up by HCl coordinated to skeletal nitrogen. [b] These polymers showed a T_g-like transition attributed to Si–O–Si motion. For details see the section in the text on thermal properties.

The ^{31}P NMR spectra for **15** and **16** contained signals corresponding to the presence of both $NP(NHR)_2$ and $NP(NHR)(OCH_2CH_2OCH_2CH_2OCH_3)$ groups as a broad singlet between −2.0 and −3.5 ppm. The spectra derived from polymers **17** and **18** contained peaks at −8.0 ppm that were consistent with the presence of $NP(OCH_2CH_2OCH_2CH_2OCH_3)_2$ groups. When the amino substituent was present in approximately 25% loading, the polymers **17** and **18** were amorphous, adhesive elastomers. Polymers with the higher content of the aminosiloxane (**15** and **16**) were rigid, amorphous materials. The thermal characteristics and surface properties will be discussed later.

(D) Mixed-Substituent Polymers Containing the Phenoxy Group. The single substituent polymer poly(diphenoxyphosphazene), $[NP(OPh)_2]_n$, is a hydrophobic, microcrystalline (T_m = 360 °C) fiber- and film-forming polymer with a T_g of −6 °C.[15] The high T_g, relative to $[NP(OCH_2CF_3)_2]_n$ and $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$, is attributed to the steric hindrance of the phenoxy groups that raises the energy barrier to torsional motions of the phosphazene backbone. These steric effects are also evident from the forcing conditions required to bring about full replacement of all the chlorine atoms in $[NPCl_2]_n$ by sodium phenoxide.[11]

As in the previous two examples, two polyphospha-

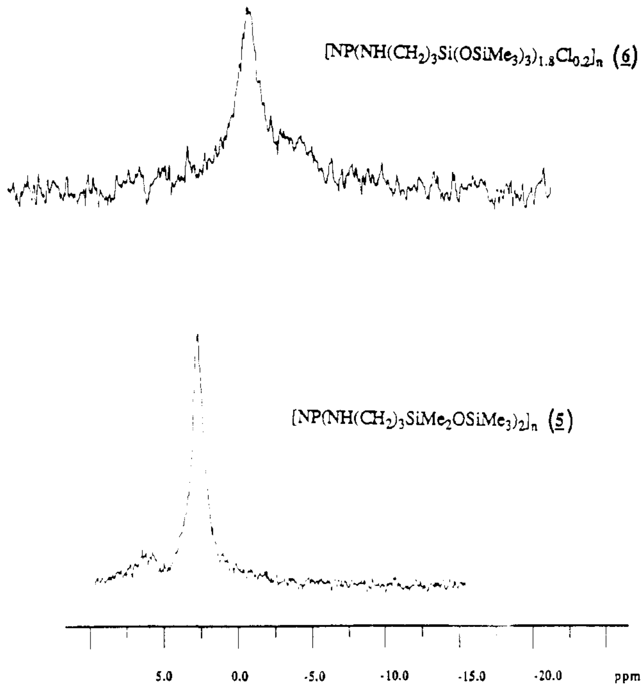


Figure 1. 36.2-MHz ^{31}P NMR spectra for polymers **5** and **6**. The broad, upfield chemical shift for **6** is indicative of incomplete substitution.

zenes with different ratios of phenoxy to chloro groups (**19** and **20**) were synthesized. Each polymer was then allowed to react with excess aminosiloxane to bring about chlorine replacement and generate polymers **21–24**. However, unlike the previous reactions, some difficulty was experienced in obtaining complete replacement of the chlorine atoms by both of the amines. Polymers **21**, **23**, and **24** underwent complete halogen replacement by both amines (see elemental analysis data, Table II). Polymer **22** was found to contain about 10% unreacted chlorine, despite the fact that the precursor polymer **19** possessed a considerable percentage of unhindered, *gem*-$NPCl_2$ units together with randomly dispersed NP(OPh)(Cl) units.[18] The reaction between $H_2N(CH_2)_3Si(OSiMe_3)_3$ and **20** paralleled the results obtained from the reactions between $H_2N(CH_2)_3Si(OSiMe_3)_3$ and cyclic trimer **1** or polymers **4** and **13** (i.e. some chlorine remained unreacted). From these results, it appears that a *gem*-$NP(NH(CH_2)_3Si(OSiMe_3)_3)_2$ unit is more sterically hindered than a $NP(OR)_2$ unit (R = OPh or $OCH_2CH_2OCH_2CH_2OCH_3$). Characterization data are listed in Tables II and III.

Polymer Characterization and Properties. All the polymers were purified by multiple reprecipitations from THF into water and into ethanol/hexane (4:1) except where noted in Table IV. Interestingly, the polymers that contained even small amounts of the aminosiloxane side groups were at least partially soluble in hexane.[19] The single substituent polymers $[NP(OCH_2CF_3)_2]_n$, $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$, $[NP(OPh)_2]_n$, and $[NP(NH(CH_2CH_2CH_3)_2]_n$ are totally insoluble in this solvent.

The purified polymers were studied by a combination of ^1H NMR integration and elemental analysis. The integration was used to estimate the ratio of aliphatic protons to methylsilyl protons. Theoretical elemental analysis values were calculated from this estimated stoichiometry. In most cases, the elemental analysis values corresponded closely to the theoretical values listed in Table IV.

Details of the Substitution Patterns. The ^{31}P NMR data were useful for elucidating the distribution of the substituents along the polymer chains. As shown in Table III, all polymers that contained 25% of an alkoxy substituent and 75% of the aminosiloxy substituent gave only one broad signal in the ^{31}P NMR spectrum. Conversely, the polymers with 75% of an alkoxy substituent and 25% of an aminosiloxy substituent generated two relatively sharp resonances in the ^{31}P NMR spectrum. This difference is a consequence of different substitution patterns that occur when a deficiency of a nucleophile is allowed to react with poly(dichlorophosphazene).

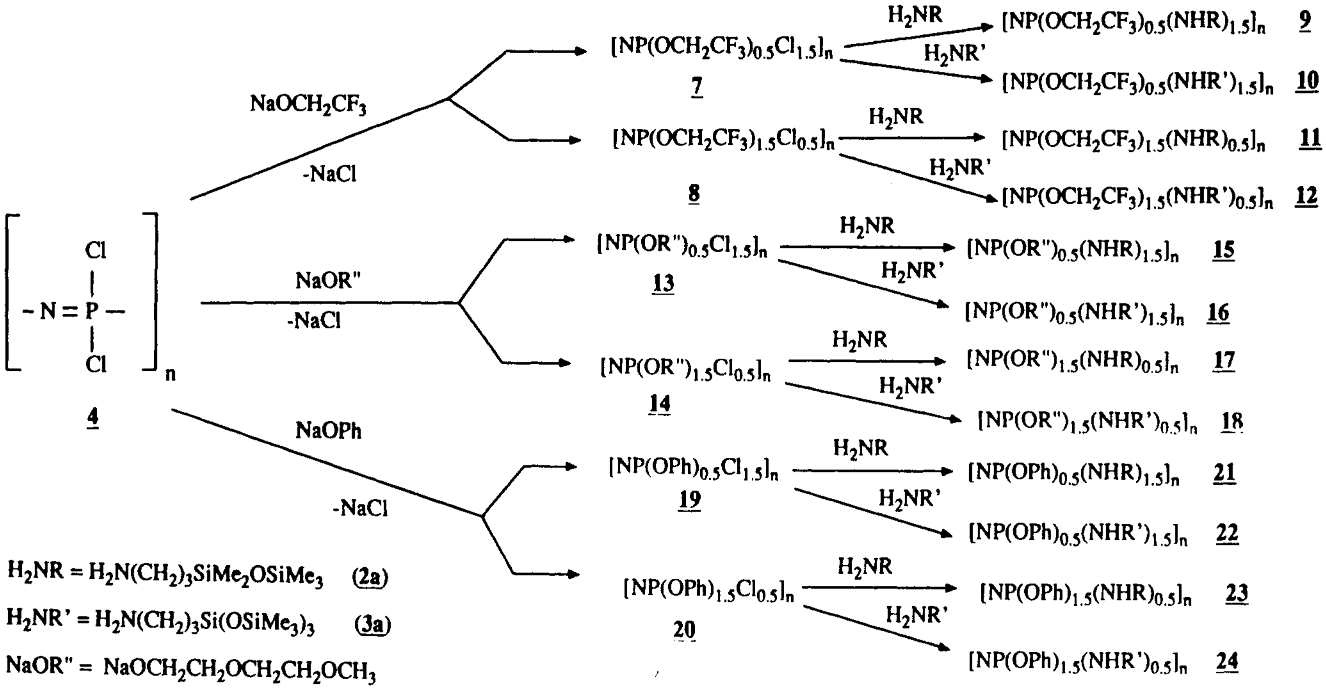
In the first possibility (Figure 2a–c), polymer **4** (Figure 2a) is exposed to only 25% of the first nucleophile (in this case, the trifluoroethoxide ion was used). Random replacement of chlorine atoms by the nucleophile generates a side group distribution in which, on the average, 25% NP(Cl)(OR) units are randomly distributed between 75% $NPCl_2$ units. The ^{31}P NMR spectrum (Figure 2b) of this species reflects this distribution in the form of two broad signals between −12.0 and −18.0 ppm, respectively. After this polymer has reacted with excess amine (H_2NR), the molecule contains $NP(NHR)_2$ units with randomly distributed NP(OR)(NHR) units. As a result, the ^{31}P NMR spectrum is similar to that of a single-substituent aminophosphazene. However, the signal is broadened and shifted slightly toward the $NP(OR)_2$ region due to the presence of NP(NHR)(OR) units (see Figure 2c).

In the second possibility, replacement of 75% of the chlorine atoms in **4** by an alkoxide ion leads to the spectra depicted in Figure 3a–c. Because of the higher loading of the initial organic side group, the phosphazene backbone must contain $NP(OR)_2$ and NP(OR)Cl units. However, in this instance, a significant number of $NP(OR)_2$ units must be flanked by other $NP(OR)_2$ units. Therefore, blocks of $NP(OR)_2$ units exist and these blocks resemble the repeat unit of a $[NP(OR)_2]_n$ homopolymer (where δ would be −8.2 ppm). However, the chemical shift of this polymeric species (see Figure 3b) is upfield from the −8.2 ppm region because of the presence of residual phosphorus chlorine bonds. Only after this species has been exposed to an excess of the aminosiloxane, can the two significantly different phosphorus environments be detected. These are units that contain blocks of $NP(OR)_2$ (δ = −8.2 ppm) and those with NP(OR)(NHR) units (δ = −1.8 ppm).

These two types of ^{31}P NMR patterns were found for all the mixed-substituent polymers. However, it is less clear how this distribution of substituents affects the bulk properties of the polymers. One generalization can be made: although each system showed unique thermal and surface properties (to be discussed later), those polymers with 75% alkoxy and 25% aminosiloxane units were adhesive, film-forming elastomers while those with 25% alkoxy units and 75% aminosiloxane units were rigid, amorphous materials. The increased rigidity of these polymers may reflect the ability of the amino side groups to hydrogen bond to their neighbors.

Thermal Properties. The glass transition temperatures (T_g) were determined by differential scanning calorimetry (DSC) and are listed in Table II. Polymers **5** and **6** gave only one T_g transition at −67 and −128 °C, respectively (see Table II). The thermogram for **6** was nearly identical with that of poly(dimethylsiloxane). Despite the similarity between the thermal transitions of **6** (T_g = −128 °C, T_c = −88 °C, and T_m = −55 °C) and poly(dimethylsiloxane), the polymer was a rigid, amorphous material with low cohesive properties rather than

Scheme III



a) The ratios of the cosubstituents shown (i.e. 0.5 : 1.5 or 1.5 : 0.5) are the target ratios. As shown in Table II, some variations from these ratios did occur. For example, polymer 23 had OPh: NHR ratio of 1.6:0.4

an elastomer. The physical characteristics of **6** more closely resembled those of poly[bis(*n*-propylamino)phosphazene], even though no similar thermal transition was detected.[20] The "brittle" character of the polymer may be a result of hydrogen bonding. This would stiffen the polyphosphazene chains while not restricting the flexibility of the siloxane side group.

Polymers **10**, **12**, **16**, **18**, and **22**, which contain the *branched* aminosiloxane $HN(CH_2)_3Si(OSiMe_3)_3$, gave two thermal transitions, one in the range of −130 to −127 °C (similar to that of **6**) and the other near the T_g of the corresponding homopolymers $[NP(OCH_2CF_3)_2]_n$ (T_g = −66 °C), $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (T_g = −84 °C), or $[NP(OC_6H_5)_2]_n$ (T_g = −6 °C). The DSC thermogram of **18** is typical of the type of thermal transitions given by these cosubstituent polymers (see Figure 4). Two thermal transitions for this polymer were detected at −128 and −77 °C. The transition at −128 °C probably represents the reordering of the siloxane side group and *not* the torsional motion of the phosphazene backbone. The second transition, at −77 °C, is in the region of the T_g for $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ and possibly represents torsional motions of the phosphazene backbone. From these thermal data, it appears that the (methoxyethoxy)ethoxy side group and the siloxane side group undergo independent thermal motions.[21,22] Double thermal transitions were found for all the polymers that contained the $HN(CH_2)_3Si(OSiMe_3)_3$ side group, except for **24**. Polymer **24** gave only one transition at −11 °C. This is perhaps due to the higher loading of the phenoxy side group, which may sterically restrict the motions of the siloxane side group.

The polymers that contained $HN(CH_2)_3SiMe_2OSiMe_3$ units were found to have only one detectable T_g. The T_g's detected for **11**, **17**, and **23** (i.e. those with 25% $HN(CH_2)_3SiMe_2OSiMe_3$) were the same as or lower then the T_g's found for the corresponding single substituent polymers $[NP(OCH_2CF_3)_2]_n$ (−66 °C), $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ (−84 °C), and $[NP(OPh)_2]_n$ (−6 °C). Specifically, the incorporation of $HN(CH_2)_3SiMe_2OSiMe_3$ units into the polymer had a "plasticizing" effect that lowered the T_g. No siloxane-related transitions were detected for polymers **5**, **9**, **11**, **15**, **17**, and **23**. This may reflect the less branched nature of the $HN(CH_2)_3SiMe_2OSiMe_3$ side group. Because this side group contains only *one* Si–O–Si unit, the siloxane function is considerably more dilute then in the case of the $HN(CH_2)_3Si(OSiMe_3)_3$ side group which contains *three* Si–O–Si units. Thus, any siloxane motion from the $HN(CH_2)_3SiMe_2OSiMe_3$ side group may not be detected by DSC experiments.

Surface Analysis. The surface characteristic of a material may be studied by measurement of the surface contact angle.[23] This method provides a rapid assessment of the surface character of a polymer film. Because of the importance of surface properties in the field of biomaterials, it was of interest to obtain information on how the siloxane substituent affected the surface characteristics of the polymers synthesized in this work.

The surface contact angles were measured by the method described in the Experimental Section and are listed in Table III. It was found that the contact angles varied from 111° (**23**) to 98° (**16**). No direct correlation between the polymer structure and the contact angle could be deduced.[24] For example, **5** contained the hydrophobic $SiMe_2OSiMe_3$ unit. However, it generated a surface contact angle that was indistinguishable from that of poly[bis(*n*-propylamino)phosphazene]. This suggests that the siloxane units may be buried beneath the surface.[23] However, polymers **23** and **24** clearly showed a more hydrophobic character than $[NP(OPh)_2]_n$, and this can be attributed to the presence of the siloxane portion of the side group. The trifluoroethoxy/aminosiloxane polymers showed either a hydrophilic enhancement (**10** and **11**) or

Table III
^{1}H NMR, ^{31}P NMR, IR, and Surface Contact Angles for Polymers

compound	signal	^{1}H NMR,[a] ppm	signal	^{31}P NMR, ppm	contact angle, deg	IR peaks,[b] cm^{-1}
$[\mathrm{NP(NH(CH_2)_3SiMe_2OSiMe_3)_2}]_n$ (**5**)	$\mathrm{N}\mathit{H}$	1.9 (1 H)	$\mathrm{NP(NHR)_2}$[d]	3.5	96.0	3450, 2930, 1254, 1150, 1050, 800
	$\mathrm{N}\mathit{CH}_2$	2.8 (2 H)				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.30 (2 H)				
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.4 (2 H)				
	$\mathrm{SiMe_2OSiMe_3}$	0.05 (15 H)				
$[\mathrm{NP(NH(CH_2)_3Si(OSiMe_3)_3)_{1.8}Cl_{0.2}}]_n$ (**6**)	$\mathrm{N}\mathit{H}$	1.8 (1 H)	$\mathrm{N}\mathit{P}\mathrm{(NHR')_2}$	−1.5	98.0	3450, 2938, 1257, 1160, 1060, 798
	$\mathrm{N}\mathit{CH}_2$	2.8 (2 H)	$\mathrm{N}\mathit{P}\mathrm{(NHR')Cl}$	−2.5		
	$\mathrm{NCH_2}\mathit{CH}_2$	1.30 (2 H)				
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.5 (2 H)				
	$\mathrm{Si(OSiMe_3)_3}$	0.04 (27 H)				
$[\mathrm{NP(OCH_2CF_3)_{0.5}(NH(CH_2)_3SiMe_2\text{-}OSiMe_3)_{1.5}}]_n$ (**9**)	$\mathit{N}\mathrm{H}$	1.0	$\mathrm{N}\mathit{P}\mathrm{(NHR)_2}$	−0.9	105.0	3450, 2930, 1254, 1157, 1070, 802
	$\mathrm{N}\mathit{CH}_2$	2.8				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.5	$\mathrm{N}\mathit{P}\mathrm{(NHR)(OCH_2CF_3)}$			
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.5				
	$\mathrm{SiMe_2OSiMe_3}$	0.1 (20 H)				
	$\mathrm{O}\mathit{CH}_2\mathrm{CF_3}$	4.3 (0.8 H)				
$[\mathrm{NP(OCH_2CF_3)_{0.6}(NH(CH_2)_3Si(OSi\text{-}Me_3)_3)_{1.35}}]_n$ (**10**)	$\mathrm{N}\mathit{H}$	1.2	$\mathrm{N}\mathit{P}\mathrm{(NHR')_2}$	−2.1	97.8	3450, 2930, 1250, 1204, 1057, 802
	$\mathrm{N}\mathit{CH}_2$	2.7				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.3	$\mathrm{N}\mathit{P}\mathrm{(NHR')(OCH_2CF_3)}$			
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.3				
	$\mathrm{Si(OSiMe_3)_3}$	0.1 (33.2 H)				
	$\mathrm{O}\mathit{CH}_2\mathrm{CF_3}$	4.1 (0.8 H)				
$[\mathrm{NP(OCH_2CF_3)_{1.5}(NH(CH_2)_3SiMe_2\text{-}OSiMe_3)_{0.5}}]_n$ (**11**)	$\mathrm{N}\mathit{H}$	1.5	$\mathrm{N}\mathit{P}\mathrm{(NHR)(OCH_2CF_3)}$	−1.8	99.9	3360, 2955, 1254, 1057, 842, 802
	$\mathrm{N}\mathit{CH}_2$	2.9				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.5	$\mathrm{N}\mathit{P}\mathrm{(OCH_2CF_3)_2}$	−8.2		
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.5				
	$\mathrm{SiMe_2OSiMe_3}$	0.1 (9 H)				
	$\mathrm{O}\mathit{CH}_2\mathrm{CF_3}$	4.4 (2.8 H)				
$[\mathrm{NP(OCH_2CF_3)_{1.5}(NH(CH_2)_3Si\text{-}(OSiMe_3)_3)_{0.5}}]_n$ (**12**)	$\mathrm{N}\mathit{H}$	1.20	$\mathrm{N}\mathit{P}\mathrm{(NHR')(OCH_2CF_3)}$	−1.2	107.1	3460, 2957, 1257, 1150, 1068, 840, 800
	$\mathrm{N}\mathit{CH}_2$	2.7				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.3	$\mathrm{N}\mathit{P}\mathrm{(OCH_2CF_3)}$	−8.3		
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.3				
	$\mathrm{Si(OSiMe_3)_3}$	0.1 (13.5 H)				
	$\mathrm{O}\mathit{CH}_2\mathrm{CF_3}$	4.1 (3.0 H)				
$[\mathrm{NP(MEE)_{0.5}(NH(CH_2)_3SiMe_2\text{-}OSiMe_3)_{1.5}}]_n$ (**15**) (MEE = $\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}$)	$\mathrm{N}\mathit{H}$	1.1	$\mathrm{N}\mathit{P}\mathrm{(NHR)_2}$	−2.1	98.0	3360, 2960, 1254, 1160, 1050, 850, 800
	$\mathrm{N}\mathit{CH}_2$	2.8				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.4	$\mathrm{N}\mathit{P}\mathrm{(NHR)(MEE)}$			
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.4				
	$\mathrm{SiMe_2OSiMe_3}$	0.1 (22.5 H)				
	$\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}$	4.2–3.4 (5.5 H)				
$[\mathrm{NP(MEE)_{0.5}(NH(CH_2)_3Si(OSi\text{-}Me_3)_3)_{1.35}}]_n$ (**16**)	$\mathrm{N}\mathit{H}$	1.2	$\mathrm{N}\mathit{P}\mathrm{(NHR')_2}$	−3.7	98.0	3357, 2950, 1248, 1165, 1040, 842, 798
	$\mathrm{N}\mathit{CH}_2$	2.8				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.4	$\mathrm{N}\mathit{P}\mathrm{(NHR')(MEE)}$			
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.3				
	$\mathrm{Si(OSiMe_3)_3}$	0.1 (36.5 H)				
	$\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}$	4.1–3.3 (5.5 H)				
$[\mathrm{NP(MEE)_{1.5}(NH(CH_2)_3SiMe_2\text{-}OSiMe_3)0.5}]_n$ (**17**)	$\mathrm{N}\mathit{H}$	1.2	$\mathrm{N}\mathit{P}\mathrm{(NHR)(MEE)}$	0.5	98[c]	3360, 2960, 1254, 1170, 1060, 840, 798
	$\mathrm{N}\mathit{CH}_2$	2.7				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.3	$\mathrm{N}\mathit{P}\mathrm{(MEE)_2}$	−8.1		
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.3				
	$\mathrm{SiMe_2OSiMe_3}$	0.1 (9 H)				
	$\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}$	4.2–3.4 (15.4 H)				
$[\mathrm{NP(MEE)_{1.5}(NH(CH_2)_3Si(OSi\text{-}Me_3)_3)_{0.5}}]_n$ (**18**)	$\mathrm{N}\mathit{H}$	1.2	$\mathrm{N}\mathit{P}\mathrm{(NHR')(MEE)}$	−0.8	98.0	3360, 2963, 1257, 1173, 1057, 843, 803
	$\mathrm{N}\mathit{CH}_2$	2.8				
	$\mathrm{NCH_2}\mathit{CH}_2$	1.6	$\mathrm{N}\mathit{P}\mathrm{(MEE)_2}$	−8.0		
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.3				
	$\mathrm{Si(OSiMe_3)_3}$	0 (13.5 H)				
	$\mathrm{OCH_2CH_2OCH_2CH_2OCH_3}$	4.2–3.3 (16.5 H)				
$[\mathrm{NP(OC_6H_5)_{0.5}(NH(CH_2)_3SiMe_2\text{-}OSiMe_3)_{1.5}}]_n$ (**21**)	$\mathrm{N}\mathit{H}$	1.0				3380, 3065, 2950, 1254, 1190, 1070, 1050, 840, 800
	$\mathrm{N}\mathit{CH}_2$	2.6	$\mathrm{N}\mathit{P}\mathrm{(NHR)_2}$	+2.0	102.0	
	$\mathrm{NCH_2}\mathit{CH}_2$	1.3				
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.4	$\mathrm{N}\mathit{P}\mathrm{(NHR)(OC_6H_5)}$	−2.0		
	$\mathrm{SiMe_2OSiMe_3}$	0.1 (24 H)				
	$\mathrm{OC_6H_5}$	7.2–6.9 (2 H)				
$[\mathrm{NP(OC_6H_5)_{0.55}(NH(CH_2)_3Si\text{-}(OSiMe_3)_3)_{1.25}}]_n$ (**22**)	$\mathrm{N}\mathit{H}$	1.7			105.1	3360, 3060, 2940, 1253, 1170, 1060, 840, 798
	$\mathrm{N}\mathit{CH}_2$	2.6	$\mathrm{N}\mathit{P}\mathrm{(NHR')_2}$	−4.0		
	$\mathrm{NCH_2}\mathit{CH}_2$	1.4				
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.2	$\mathrm{N}\mathit{P}\mathrm{(NHR')(OC_6H_5)}$			
	$\mathrm{Si(OSiMe_3)_3}$	0 (33.8 H)				
	$\mathrm{OC_6H_5}$	7.2–7.0 (2.8 H)				
$[\mathrm{NP(OC_6H_5)_{1.4}(NH(CH_2)_3\text{-}SiMe_2OSiMe_3)_{0.6}}]_n$ (**23**)	$\mathrm{N}\mathit{H}$	1.3				3380, 3045, 2930, 1260, 1180, 1050, 840, 800
	$\mathrm{N}\mathit{CH}_2$	2.5	$\mathrm{N}\mathit{P}\mathrm{(NHR)(OC_6H_5)}$	−5.5	111.3	
	$\mathrm{NCH_2}\mathit{CH}_2$	0.8				
	$\mathrm{NCH_2CH_2}\mathit{CH}_2$	0.2	$\mathrm{N}\mathit{P}\mathrm{(OC_6H_5)_2}$	−18.1		
	$\mathrm{SiMe_2OSiMe_3}$	0.1 (16.2 H)				
	$\mathrm{OC_6H_5}$	7.2–6.9 (7 H)				

Table III (Continued)

compound	signal	^{1}H NMR,[a] ppm	signal	^{31}P NMR, ppm	contact angle, deg	IR peaks,[b] cm^{-1}
$[NP(OC_6H_5)_{1.5}(NH(CH_2)_3Si(OSiMe_3)_3)_{0.5}]_n$ (**24**)	N*H*	1.7	N*P*(NHR′)(OC_6H_5)	−6.0	105.4	3360, 3030, 2940, 1257, 1173, 1050, 840, 798
	N*CH_2*	2.6				
	NCH_2*CH_2*	1.4				
	NCH_2CH_2*CH_2*	0.2	N*P*$(OC_6H_5)_2$	−18.0		
	$Si(OSiMe_3)_3$	0 (13.5 H)				
	OC_6H_5	7.2–7.0 (7.5 H)				

[a] All ^{1}H NMR data were recorded for solutions in $CDCl_3$. The signals were broad because of the high solution viscosity. The numbers in parentheses represent integrated ratios. [b] IR samples were taken from thin films cast onto NaCl plates. [c] The surface contact angle changed from ≃98° to ≃75° over a period of time. [d] NHR = $HN(CH_2)_3SiMe_2OSiMe_3$ and NHR′ = $HN(CH_2)_3Si(OSiMe_3)_3$.

Table IV
Conditions for Polymer Synthesis[b]

compd	4, mmol	THF, mL	NaOR, mmol	Et_3N, mmol	H_2NR, mmol	reactn time, h	purificatn solvents
9	34.5	150	8.6	260.0	38.9	12	methanol, H_2O
10	17.3	70	4.3	130.0	26.0	8	ethanol/hexane, H_2O[a]
11	34.5	120	25.9	86.0	13.1	12	ethanol/hexane, H_2O
12	34.5	120	25.9	86.3	8.6	10	ethanol/hexane, H_2O
15	34.5	120	8.6	260.0	38.9	10	methanol, H_2O
16	34.5	120	8.6	260.0	40.0	8	ethanol/hexane, H_2O
17	51.7	150	38.8	130.0	19.4	12	ethanol, CH_3CN, H_2O
18	34.5	120	25.9	86.3	8.6	8	CH_3CN, H_2O
21	34.5	120	8.6	260.0	38.9	8	methanol, H_2O
22	17.3	70	4.3	130.0	26.0	8	methanol/hexane, H_2O
23	17.3	70	13.0	86.3	20.0	36	ethanol/hexane, H_2O
24	17.3	70	13.0	86.3	8.6	20	ethanol/hexane, H_2O

[a] Those purification solvents listed as ethanol/hexane were in an approximate ratio of 4:1 by volume. [b] Polymers **7**, **8**, **13**, **14**, **19**, and **20** were hydrolytically unstable reactive intermediates that were used in situ.

a hydrophobic enhancement (**12**) compared to $[NP(OCH_2CF_3)_2]_n$.

It is easier to understand these results if the aminosiloxane side group is considered to be an amphiphile. Thus, a hydrophilic enhancement would result if the amino portion were oriented toward the surface, whereas hydrophobic enhancement would result if the siloxane units were concentrated at the surface. Yasuda and Sharma[23] concluded that the surface properties of a polymer are more a function of *surface* orientation and side group mobility rather than the *bulk* hydrophilic/hydrophobic nature of the side groups. Our preliminary results for these systems agree with their conclusions. Further surface analysis of these systems is needed to fully understand what effect these side groups have on the surface microstructure.

Conclusion

The preparation of polyphosphazenes that contain aminosiloxane side groups has provided access to novel macromolecular systems with unusual combinations of properties. Although other siloxane/phosphazene systems have been reported,[25,26] their hydrolytic instability[27] or modest loading[4,7,8] of the siloxane side groups has limited their usefulness. As demonstrated in this paper, a wide variety of high molecular weight poly(aminosiloxyphosphazenes) are accessible. Their ease of preparation, the higher loading of siloxane groups, and the possibility of control over the final side group stoichiometry has generated a new series of poly(organophosphazenes) with properties that are attractive for further exploration.

Experimental Section

Equipment. ^{31}P (36.2 MHz) NMR spectra were obtained with the use of a JEOL FX90Q spectrometer. Chemical shifts are reported in parts per million relative to 85% H_3PO_4 at 0 ppm. High-field NMR spectra were obtained with the use of a Bruker WP 200-MHz or a Bruker AM 300-MHz spectrometer. Chemical shifts are referenced to external TMS at 0 ppm. A pulse delay of 10 s was employed to ensure that the integrated intensities were accurate. Infrared spectra were obtained with the use of a Perkin-Elmer Model 1710 FT-IR spectrophotometer. Glass transition temperatures were recorded by using a Perkin-Elmer DSC 7 unit. Samples weights were between 4 and 8 mg. The samples were heated to 125 °C to remove traces of solvents and were then cooled rapidly to −145 °C. The measurements were made at a heating rate of 10 °C/min. Small-molecule products were purified by gravity column chromatography over silica gel (60/200 mesh). Compounds were eluted with grease-free hexanes and methylene chloride purified by distillation. Polymer molecular weights were estimated by means of a Hewlett-Packard 1090 liquid chromatography unit. A calibration curve was established by comparison with known molecular weight polystyrene and poly[bis(trifluoroethoxy)phosphazene] samples. Samples were prepared at a concentration of approximately 2% w/w in THF. Surface contact angles were measured with the use of a Rame-Hart contact angle goniometer. Dust-free films were prepared by solution casting onto glass slides from concentrated THF solution. The values reported are accurate to within +/−1 °C. The angles were measured by using 1-μL drops of deionized water in an atmosphere of 100% humidity. The data were measured within 1 min of applying the drop and again after 10 min. The reported values represent an average of at least eight measurements.

Materials and Procedures. All reaction mixtures were protected by an atmosphere of dry argon (Matheson) using standard Schlenk line techniques. Tetrahydrofuran (THF, Omnisolv) and dioxane (Omnisolv) were dried before use by distillation from sodium benzophenone ketyl under an atmosphere of dry argon. 2,2,2-Trifluoroethanol (Halocarbon) and (methoxyethoxy)ethanol (Aldrich) were purified and dried by fractional distillation from BaO under an atmosphere of dry argon. Dry phenol (Aldrich) was obtained by azeotropic distillation from benzene. Triethylamine (Aldrich) was refluxed with CaH_2 for 12 h under an atmosphere of argon before use. Chloroplatinic acid hexahydrate (Aldrich) was used as received. (3-Aminopropyl)tris(trimethylsiloxy)silane, $H_2N(CH_2)_3Si(OSiMe_3)_3$, (*N*-trimethylsilyl)allylamine, $Me_3SiNHCH_2CH{=}CH_2$, and pentamethyldisiloxane, $HSiMe_2OSiMe_3$, were available from Petrarch and were purified by distillation [bp 60–62 °C (0.1 mmHg), 110–112 °C, and 86–88 °C, respectively]. $H_2N(CH_2)_3SiMe_2OSiMe_3$ and $H_2N(CH_2)_3Si(OSiMe_3)_3$ were dried by vacuum fractional distillation from BaO. Hexachlorocyclotriphosphazene (Ethyl Corp.) was purified by recrystallization

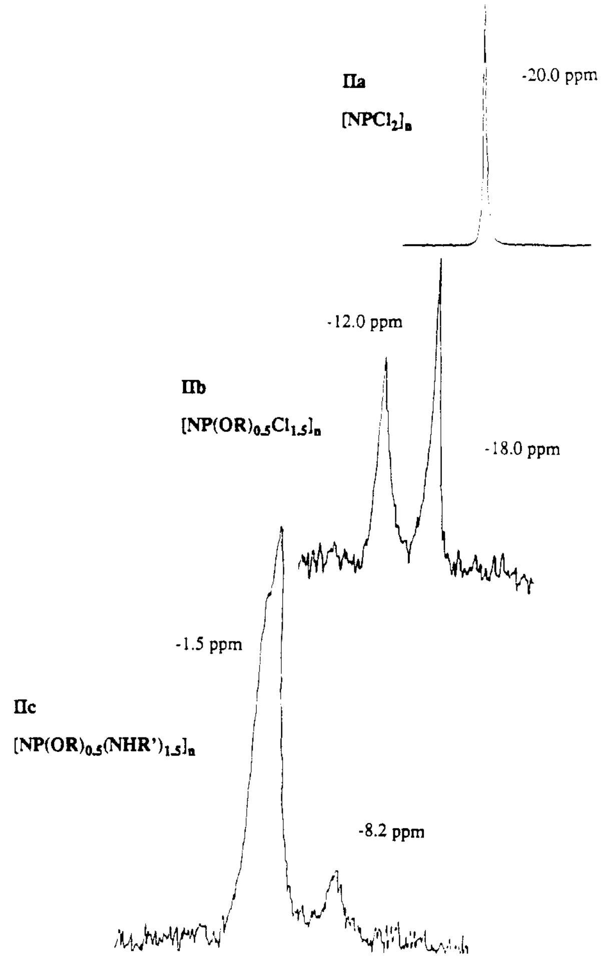


Figure 2. a–c. ^{31}P NMR spectra derived from the reaction of 4 with 25% sodium trifluoroethoxide, followed by reaction with excess amine. Note the small percentage of gem substitution at −8.2 ppm (c) due to the nature of the trifluoroethoxide ion, see reference 16.

from hexane and by sublimation [30 °C (0.25 mmHg)]. Poly(dichlorophosphazene) was prepared as described previously.[8] Elemental microanalyses were obtained by Galbraith Laboratory, Knoxville, TN.

Synthesis of (3-Aminopropyl)pentamethyldisiloxane. A slightly modified procedure derived from ref 14 was employed. In a typical experiment freshly distilled (*N*-trimethylsilyl)allylamine (25.0 g, 0.19 mol) was mixed with freshly distilled pentamethyldisiloxane (28.1 g, 0.18 mol). To this was added THF (~100 mL) and chloroplatinic acid hexahydrate (0.5 g, 1.2 mmol, 0.5 mol %). The reaction mixture was refluxed for about 8 h or until no Si–H stretching peak in the infrared spectrum at ~2145 cm^{-1} could be detected. The reaction mixture was then cooled to room temperature, and a large excess of 95% ethanol (~50 mL) was added. The reaction mixture was then refluxed for about 8 h to remove the *N*-trimethylsilyl protecting group. The product was isolated by vacuum distillation and purified by vacuum fractional distillation from BaO [bp 38–40 °C (0.1 mmHg)]. ^{13}C NMR ($CDCl_3$, 22.5 MHz); 45.3 ppm, H_2NC; 27.5 ppm, H_2NCC; 15.0 ppm, *C*Si; 0.2, 3.2 ppm, $Si(CH_3)_2$ and $Si(CH_3)_3$. Typical yields were between 55% and 80%. Additional characterization data are listed in Table I.

Synthesis of $N_3P_3(OPh)_5Cl$ (1). Freshly sublimed $N_3P_3Cl_6$ (10.0 g, 0.03 mol) was dissolved in 350 mL of dry THF and was stirred under an atmosphere of dry argon. To this solution was added 5.1 equiv of sodium phenoxide prepared by the interaction of dry phenol (14.4 g, 0.15 mol) with sodium metal (3.5 g, 0.15 mol) in THF (100 mL). The addition of sodium phenoxide to $N_3P_3Cl_6$ took place during a 1-h period. The reaction mixture was then refluxed for 24 h. The THF was removed under reduced pressure to produce a light brown oil. The oil was purified by column chromatography on silica gel using hexanes/CH_2Cl_2 (5:1). The purified oil solidified in pentane at 0 °C and was recrystallized from warm methanol, mp 60–62 °C. ^{31}P NMR ($CDCl_3$, 36.2 MHz); AB_2, *P*(OPh)Cl, 20.2 ppm; $P(OPh)_2$, 8.6 ppm, J_{PNP} = 87.2 Hz.

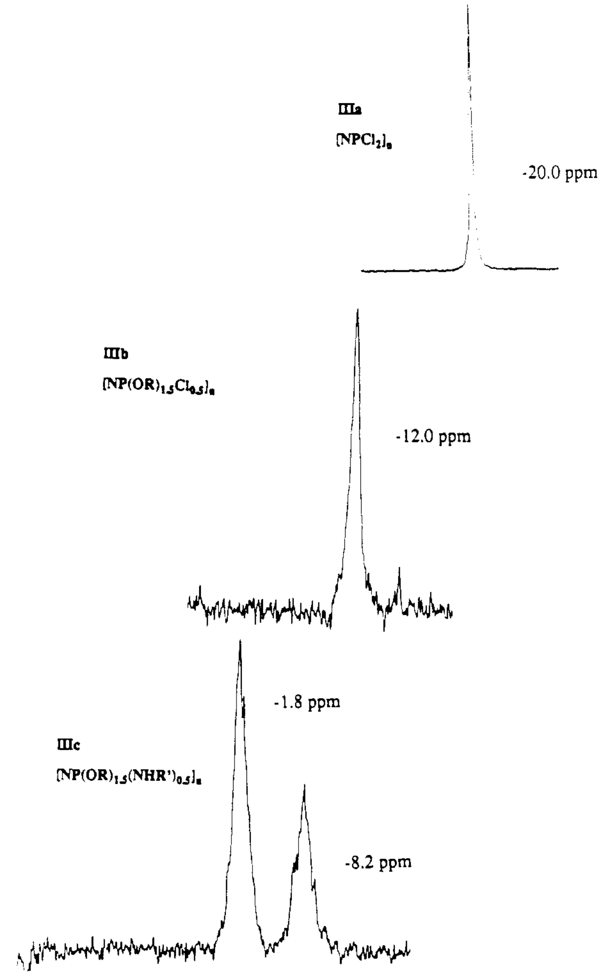


Figure 3. a–c. ^{31}P NMR spectra derived from the reaction of 4 with 75% sodium trifluoroethoxide. The increased intensity of the signal at −8.2 ppm is because of blocks of $[NP(OCH_2CF_3)_2)]_n$ units in the backbone of the polymer.

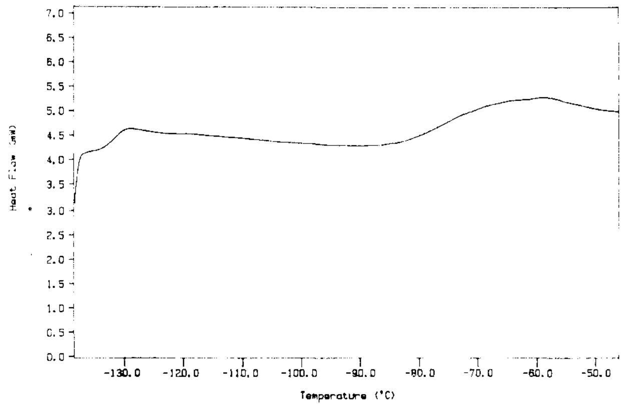


Figure 4. DSC thermogram for polymer 18. The two thermal transitions are associated with siloxane side-group motion (−128 °C) and $[NP(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ backbone torsional motion (−77 °C).

Synthesis of $N_3P_3(OPh)_5NH(CH_2)_3SiMe_2OSiMe_3$ (2). To a solution of 1 (1.0 g, 1.57 mmol) in dry THF (70 mL) was added an excess of triethylamine (1.5 g, 15 mmol). The solution was then warmed slightly. To this warm solution was added a solution of (3-aminopropyl)pentamethyldisiloxane (0.65 g, 3.1 mmol) in THF (10 mL). The reaction mixture was refluxed for 12 h, and the progress of the reaction was monitored by ^{31}P NMR spectroscopy. The ^{31}P NMR spectrum changed from an AB_2

with J_{PNP} equal to 83.9 Hz to an AB_2 with J_{PNP} equal to 76.2 Hz. The solvent was removed, and the residue was recrystallized from hexane/ethanol (4:1) at 0 °C to give **2**, mp 62–63 °C. ^{31}P NMR (THF–D_2O lock): $P(OPh)_2$, 17.7 ppm; $P(OPh)(NHR)$, 8.2 ppm, J_{PNP} = 76.2 Hz. Additional characterization data are listed in Table I.

Synthesis of $N_3P_3(OPh)_5NH(CH_2)_3Si(OSiMe_3)_3$ (3). Compound **1** (2.0 g, 3.15 mmol) was dissolved in THF in a manner similar to that described for the synthesis of **2**. Excess dry triethylamine (3.2 g, 31.5 mmol) was added, and the solution was warmed slightly. To this solution was added (3-aminopropyl)tris(trimethylsiloxy)silane (2.5 mL, 6.3 mmol, 2 equiv excess) in THF (10 mL). The reaction mixture was refluxed for approximately 1 h, before the formation of $Et_3N{:}HCl$ could be detected as a white precipitate in the reaction mixture. After the mixture had reacted for 24 h at 66 °C, the ^{31}P NMR spectrum changed from an AB_2 pattern with J_{PNP} equal to 83.9 Hz to an AB_2 with J_{PNP} equal to 76.2 Hz. The solvent was removed and the oily residue was purified by column chromatography using hexane/CH_2Cl_2 (4:1) as the eluting solvents. ^{31}P NMR (THF–D_2O lock): $P(OPh)_2$, 17.7 ppm; $P(OPh)(NHR)$, 8.2 ppm, J_{PNP} = 76.2 Hz. Additional characterization data are listed in Table I.

Synthesis of $[NP(NH(CH_2)_3SiMe_2OSiMe_3)_2]_n$ (5). Poly(dichlorophosphazene) (0.5 g, 8.62 mmol) was dissolved in THF (50 mL). Excess triethylamine (8.7 g, 86 mmol) was added, and the solution was warmed to ~50 °C. To this solution was added an excess of (3-aminopropyl)pentamethyldisiloxane (2.0 g, 9.8 mmol), and the mixture was then heated to reflux for 8 h. The reaction was monitored by ^{31}P NMR spectroscopy until no further change in the NMR spectrum was detected. The ^{31}P NMR spectrum of the reaction mixture contained a singlet centered around +3.5 ppm. The solution was concentrated, and the polymer was purified by reprecipitation from THF into water and ethanol. The characterization data are listed in Tables II and III.

General Preparation of Mixed-Substituent Polymers. The general synthetic procedure involved the preparation of a solution of poly(dichlorophosphazene) (~1.0 g) in THF (~75 mL) followed by the addition of a stoichiometric deficiency of NaOR (R = CH_2CF_3, $CH_2CH_2OCH_2CH_2OCH_3$, or Ph) in an amount designed to replace either 25% or 75% of the chlorine atoms. The reaction mixture was then refluxed gently for approximately 8–10 h and cooled to room temperature. To the partially substituted polymer was added freshly distilled, *dry* triethylamine in a 10 equiv excess of the theoretical amount of HCl to be produced. The aminosiloxane was then added as a solution in THF to the polymer. The reaction mixture was refluxed and monitored by ^{31}P NMR spectroscopy until no further change in the chemical shifts of the peaks could be detected. Typically this was accomplished in 8–12 h for the unbranched aminosiloxane and 12–36 h for the branched aminosiloxane. The polymers were isolated, purified, and characterized as described earlier. The details for each reaction are listed in Table IV.

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References and Notes

(1) This paper is the eighth from our laboratory on organosilicon derivatives of phosphazenes. For previous papers in this series see ref 2–8.

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(19) Polymer **17** was found to be insoluble in hexane. It was therefore possible to purify the polymer by precipitation from THF into hexanes and water.

(20) Polymer **6** did not show any other thermal transitions by DSC analysis above −55 °C up to its decomposition temperature of 250 °C. A T_g transition similar to the transition detected for **5** may have been present but was not detected due to the stronger T_c and T_m transitions.

(21) DSC thermograms of the primary amine $H_2N(CH_2)_3Si(OSiMe_3)_3$ and the oligosiloxane $Me_3Si–(OSiMe_2)_2–OSiMe_3$ gave a "T_g"-type transition at −118 °C. This result suggest that it is possible to detect side-group motion of short-chain species by DSC experiments. Therefore, it was concluded that the thermal transitions in the polymers around −128 °C are a consequence of siloxane side group motion and not phosphazene backbone rotation.

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Registry No. **1**, 5032-39-3; **2**, 125250-49-9; **3**, 125250-50-2; $NH_2(CH_2)_3SiMe_2OSiMe_3$, 23029-21-2; $NH_2(CH_2)_3Si(OSiMe_3)_3$, 25357-81-7.