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Synthesis and Characterization of Phosphazene Di- and Triblock Copolymers via the Controlled Cationic, Ambient Temperature Polymerization of Phosphoranimines

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ABSTRACT: An advanced process for the synthesis of polyphosphazenes with controlled architectures has been investigated. By this method, a wide range of well-defined phosphazene di- and triblock copolymers with controlled molecular weights and narrow polydispersities have been synthesized (M_n up to 4.8×10^4 with polydispersities of 1.06−1.39). The diblock copolymers, $\{[N{=}PCl_2]_n[N{=}PR(R')]_m\}$, were synthesized by the cationic condensation polymerization of the phosphoranimines, $PhCl_2P{=}NSiMe_3$, $Me(Et)ClP{=}NSiMe_3$, $Me_2ClP{=}NSiMe_3$, $Ph_2ClP{=}NSiMe_3$, and $PhF_2P{=}NSiMe_3$, at 35 °C initiated from the "living" end unit of poly(dichlorophosphazene), $[Cl-(PCl_2{=}N)_n\text{-}PCl_3{}^+PCl_6{}^-]$ which was itself formed by the polymerization of $Cl_3P{=}NSiMe_3$ with small amounts of PCl_5 initiator in CH_2Cl_2 at 25 °C. Halogen replacement reactions through the use of $NaOCH_2CF_3$ and/or $NaOCH_2CH_2OCH_2CH_2OCH_3$ on the diblock copolymers yielded fully organo-substituted macromolecules. In addition, the diblock copolymer $\{[N{=}PMe(Et)]_n[N{=}PMe(Ph)]_m\}$ was formed by the block copolymerization of the two different organophosphoranimines. Triblock species were produced by the reaction of the "living" difunctional initiator, $-\{CH_2NH(CF_3CH_2O)_2P-N-PCl_3{}^+PCl_6{}^-\}_2$, first with $Cl_3P{=}NSiMe_3$ and second with $Me(Et)ClP{=}NSiMe_3$, followed by halogen replacement with $NaOCH_2CF_3$, to yield the triblock $\{[(Et)MeP{=}N]_m[(CF_3CH_2O)_2P{=}N]_n-P(OCH_2CF_3)_2NHCH_2CH_2NH-(CF_3CH_2O)_2P-[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe(Et)]_m\}$. The evidence for the formation of the di- and triblock copolymers includes NMR, GPC, elemental analysis, and solubility data.

Introduction

Polyphosphazenes, $(N{=}PR_2)_n$, are inorganic−organic polymers in which the side group (R) can be halogeno, organo, or organometallic units. A large number of different polyphosphazenes are known, all with the same backbone structure but with different side groups attached to the phosphorus atoms of the skeleton. Different side units are normally introduced via the macromolecular replacement of the halogen atoms in poly(dichlorophosphazene), $(N{=}PCl_2)_n$, by organic groups using organic or organometallic nucleophiles. Two or more different types of side groups can be incorporated by sequential or simultaneous substitution reactions. These generate a wide range of property combinations that result from the presence of the inorganic backbone and the large number of side group permutations.[1,2] A particular challenge in this field is to develop methods for the preparation of block copolymers that contain phosphazene units. Block copolymers offer the prospect of amphiphilic materials and macromolecules with controlled compatibility with other polymers as a route to the preparation of polymer alloys and interpenetrating networks, especially in combination with conventional organic polymers.

Polyphosphazenes can be synthesized by a number of different methods. However, many of the polymerization routes allow little or no control over the molecular weight (MW) and yield polymers with broad polydispersities (PDI). The widely used ring-opening polymerization of $(NPCl_2)_3$ produces polymers with high MWs ($M_w{\sim}10^6$), but with a number of drawbacks, which include the high polymerization temperatures required to produce $(NPCl_2)_n$ (210−260 °C), the absence of molecular weight or architectural control, and the high PDIs of the polymers (up to 10 in some cases).[3] Other synthetic methods involve the condensation polymerization of organophosphoranimines. These reactions, with or without anionic initiators in the bulk state at 100−200 °C, have yielded polyphosphazenes with M_n values up to $\sim 10^5$ and polydispersities of less than 3.[4−11] Phosphazene block copolymers, such as $\{[N{=}P(OCH_2CF_3)_{1.16}(OCH_2CH_2OCH_3)_{0.84}]_n-[N{=}P(OCH_2CF_3)_2]_m\}$ derived from the monomers $(CF_3CH_2O)_3P{=}NSiMe_3$ and $(CH_3OCH_2CH_2O)(CF_3CH_2O)_2P{=}NSiMe_3$, have been synthesized by the thermal *anionic* copolymerization of these organophosphoranimines.[12−14] This method yields block copolymers in which one of the blocks has random substituents because of the two possible leaving groups on one of the phosphoranimines (e.g., $CH_3OCH_2CH_2O-$ and CF_3CH_2O-). The block copolymers produced by anionic polymerization have M_n values up to $\sim 10^5$, with PDIs of less than 2.

Recently, an ambient temperature route to polyphosphazenes was discovered in our laboratories via the solution-state living *cationic* polymerization of halophosphoranimines initiated by small amounts of PCl_5 (Schemes 1 and 2).[15−18] For example, the monomer, $Me_3SiN{=}PCl_3$ can be polymerized to $(NPCl_2)_n$ by this method. This new route has provided an improved method for the synthesis of polyphosphazenes with controlled molecular weights (M_n up to $\sim 10^5$) with low

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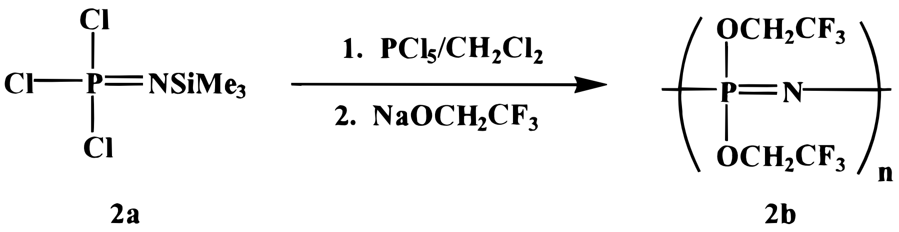
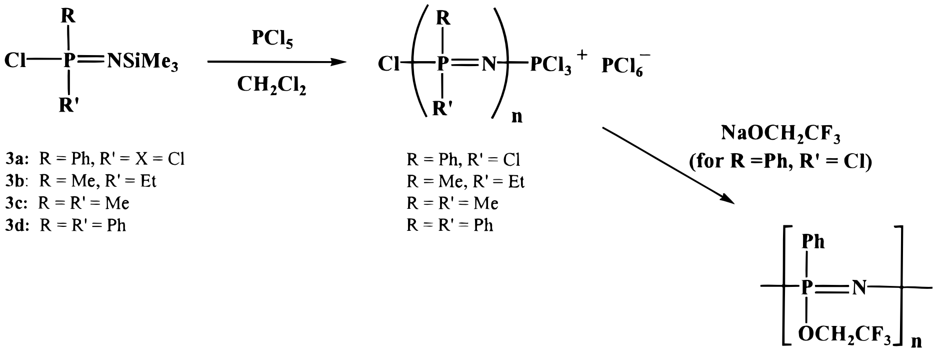
Scheme 1



Scheme 2



polydispersities (<1.3). The method has also allowed architectural control by the formation of well-defined phosphazene diblock[19] and star copolymers.[20] In addition, the diversity of the copolymers can be widened even more by replacement of the halogen atoms by organic groups. Although a large number of phosphazene polymers have been prepared via the macromolecular substitution reactions of poly(dichlorophosphazene),[1,2,21−23] phosphazene−phosphazene *block* copolymers produced by (a) the living polymerization at ambient temperatures and (b) macromolecular substitution reactions have not been reported previously. In this paper, we describe the synthesis and characterization of well-defined phosphazene di- and triblock copolymers produced via the cationic condensation polymerization of phosphoranimines.

Results and Discussion

In our earlier work, the polymerization of $Cl_3P{=}NSiMe_3$ (**2a**) with small amounts of PCl_5 initiator to form poly(dichlorophosphazene) was shown to be a living process.[16] The addition of $Cl_3P{=}NSiMe_3$ (**2a**) to living samples of poly(dichlorophosphazene), $[Cl(PCl_2{=}N)_nPCl_3]^+[PCl_6]^-$ (**1**) induced continued polymerization to give higher molecular weight forms of **1**, while the addition of end-capping phosphoranimines, such as $(CF_3CH_2O)_3P{=}NSiMe_3$, prevented further chain growth and yielded end-functionalized polymers. Other phosphoranimine monomers, such as $PhX_2P{=}NSiMe_3$ (where X = F or Cl), also showed continued polymerization when treated with more of the $PhX_2P{=}NSiMe_3$ monomer.[17,24] Here we demonstrate that the addition of a second phosphoranimine to a living polyphosphazene chain permits the synthesis of phosphazene−phosphazene block copolymers via living active sites at the termini of these polymer chains.

Overall Approach. Initial studies showed that the addition of organophosphoranimines, $PhCl_2P{=}NSiMe_3$ (**3a**), $Me(Et)ClP{=}NSiMe_3$ (**3b**), or $Me_2ClP{=}NSiMe_3$ (**3c**), in CH_2Cl_2 to living samples of **1** (formed from 10:1 to 20:1 ratios of $Cl_3P{=}NSiMe_3$ (**2a**):PCl_5 in CH_2Cl_2) resulted in the formation of chlorophosphazene-organophosphazene block copolymers, $\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$(**4a**), $\{[N{=}PCl_2]_n[N{=}PMe(Et)_m\}$(**4b**), $\{[N{=}PCl_2]_n[N{=}PMe_2]_m\}$ (**4c**).[19] The copolymers **4a**−**c** possessed repeating unit block lengths (n:m) of 20:71, 40:71, and 40:25 as determined by a combination of NMR spectroscopy (^1H and ^{31}P) and the initial **2a**:PCl_5 ratios.

However, *in solution*, the block copolymerization of the *organo*phosphoranimine monomer from the living terminus of **1** was often slow and did not proceed to completion. This gave copolymers with a second segment length shorter than planned. Moreover, the polymerization rate of the second phosphoranimine was not reproducible. Polymerization times ranged from 2 days to 2 weeks. This is a pattern found also for the solution-state homopolymerization of organophosphoranimines initiated by PCl_5 in CH_2Cl_2.[17] Thus, a modified procedure was developed to promote the polymerization of organophosphoranimines from living **1**. In this procedure the addition of the organo-monomer was followed by removal of the solvent under vacuum at 35 °C to induce a solvent-free polymerization. The reaction rates were now more reproducible, with the polymerization of the second phosphoranimine typically complete within 3 days at ambient temperatures. Moreover, the optimum temperature for each reaction could now be utilized. This process resulted in well-defined block copolymers.

Further structural diversity was achieved through halogen replacement reactions with the use of two different nucleophiles, $NaOCH_2CF_3$ and $NaOCH_2CH_2OCH_2CH_2OCH_3$, to produce a variety of derivative block copolymers. Moreover, the copolymerization of different monomers with different halogen groups, one with chlorine side units and the other with fluorine, allowed for some additional substitution opportunities. The greater reactivity of P−Cl vs P−F bonds to nucleophilic replacement allowed the selective introduction of different organic side groups into the two different blocks. Because of the special characteristics of the P−F bond, this approach should in future work allow the introduction of alkyl or aryl side groups through the use of organometallic reagents.[24] Finally, triblock copolymers

Table 1. Phosphazene Block Copolymer Data for $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PR'(R')]_m\}$ Block Copolymers from $\{[N{=}PCl_2]_n[N{=}PR'(R')]_m\}$ via Macromolecular Substitution with $NaOCH_2CF_3$

			block copolymers[a] M_w (10^{-4})			homopolymer[a,b] M_w (10^{-4})		
block copolymer	n:m (initial feed)	n:m (^{1}H NMR)	theor	actual (PDI)[b]	actual (PDI)[c]	theor	actual (PDI)	yield[d] (%)
5a-1	**2a** 0.25: **3a** 0.75	0.22:0.78	2.3	1.8 (1.13)	5.2 (1.11)	0.49	1.1 (1.11)	95.4
5a-2	**2a** 0.50: **3a** 0.50	0.45:0.55	1.9	2.7 (1.12)	5.8 (1.23)	0.97	2.0 (1.04)	82.1
5a-3	**2a** 0.57: **3a** 0.43	0.55:0.45	2.1	2.8 (1.16)	6.2 (1.22)	1.2	2.3 (1.02)	96.5
5a-4	**2a** 0.67: **3a** 0.33	0.73:0.27	1.4	2.0 (1.35)	5.6 (1.32)	0.97	1.8 (1.06)	92.4
5a-5	**2a** 0.68: **3a** 0.34	0.71:0.29	1.5	2.4 (1.15)	6.0 (1.21)	1.0	1.9 (1.06)	87.5
5b	**2a** 0.33: **3b** 0.67	0.36:0.64	1.7	1.9 (1.19)		0.97	1.4 (1.06)	72.2
5c	**2a** 0.50: **3c** 0.50	0.62:0.38	1.8	1.8 (1.14)		0.97	1.3 (1.04)	60.2
5d	**2a** 0.67: **3d** 0.33	0.76:0.24	1.3	2.0 (1.25)		0.95	1.9 (1.05)	78.8

[a] GPC chromatograms for the block copolymers are opposite in refractive index polarity with respect to homopolymer samples. [b] Molecular weights are based on polystyrene standards. [c] Absolute molecular weights determined by light scattering. [d] Yields determined after precipitation into hexanes (3×) and water (2×).

Table 2. ^{31}P NMR Data for the Phosphazene Block Copolymers

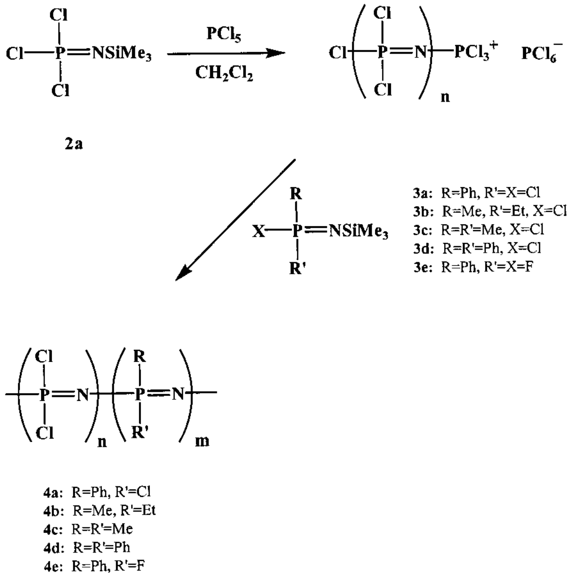
block copolymer	^{31}P NMR: δ (ppm: n; m)
$\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$ (**4a**)	−17.4; −1.0
$\{[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ (**4b**)	−17.4; 20.0
$\{[N{=}PCl_2]_n[N{=}PMe_2]_m\}$ (**4c**)	−17.4; 7.1
$\{[N{=}PCl_2]_n[N{=}PPh_2]_m\}$ (**4d**)	−17.4; −3.5
$\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**5a**)	−6.9; 3.1
$\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe(Et)]_m\}$ (**5c**)	−6.9; 20.0
$\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe_2]_m\}$ (**5c**)	−6.9; 7.1
$\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh_2]_m\}$ (**5d**)	−6.9; −3.5
$\{[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**6a**)	−6.3; −0.5
$\{[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N{=}PMe_2]_m\}$ (**6b**)	−6.3; 7.1
$\{[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N{=}PPh_2]_m\}$ (**6c**)	−6.3; −3.5

were prepared via the living process with the use of a difunctional initiator. Because of their unique architectures, these polymers are quite different from the traditional random or mixed-substituent polyphosphazenes synthesized via the reactions of two or more nucleophiles with poly(dichlorophosphazene).

Molecular Weight Analysis. Nucleophilic halogen replacement reactions carried out on the resultant halogen-containing polyphosphazenes gave derivative polymers (Schemes 1−3) that could be analyzed readily by gel permeation chromatography (GPC). The GPC results indicated that an increase in molecular weight occurred following the polymerization of the second block. The GPC molecular weights were initially estimated by a comparison to polystyrene standards, but absolute molecular weights were obtained by light scattering for a number of the copolymers. R_z values (z-radius of gyration) were generally between 10 and 30 nm for the block systems. Typically, the molecular weights were higher than the theoretically predicted values based on monomer-to-initiator ratios. Polymer aggregation in solution may account for this anomaly. Nevertheless, the GPC results, in combination with NMR spectroscopy, elemental analysis, and solubility data, indicate that the products formed are genuine block copolymers rather than separate homopolymers. The details of the synthetic and characterization work are as follows.

Phosphazene Diblock Copolymers. Trifluoroethoxy Derivative Block Copolymers (5). Living samples of **1** with chain lengths of approximately 20−40 repeat units were used as a starting point for the formation of diblock copolymers. Various amounts of the monophenyl monomer **3a** were added to the unterminated living **1** at 35 °C, followed by removal of CH_2Cl_2 and $ClSiMe_3$ to give block copolymers with the formula $\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$ (**4a**). In addition, a number of other organophosphoranimines (**3**) were copolymerized with living samples of **1** at 35 °C to produce polymers of the type $\{[N{=}PCl_2]_n[N{=}PR(R')]_m\}$ (**4**) (Scheme 3). The reaction of $NaOCH_2CF_3$ with these products (**4**) then brought about the replacement of the halogen atoms to give the fully organo-substituted species, $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PR(R')]_m\}$ (**5**) (Scheme 4, Table 1). Purification of these copolymers was accomplished by precipitation from concentrated solutions in THF or acetone into hexane and into water. NMR characterization confirmed the block copolymer structure since the characteristic NMR peaks for both of the block segments were present in the ^{1}H and ^{31}P spectra (Table 2). The results from ^{1}H NMR integration and elemental analysis agreed within experimental error, and this provided further evidence for the block structure (see Experimental Section).

Scheme 3



The GPC chromatograms for block copolymers **5** with trifluoroethoxy side groups showed a refractive index

Scheme 4

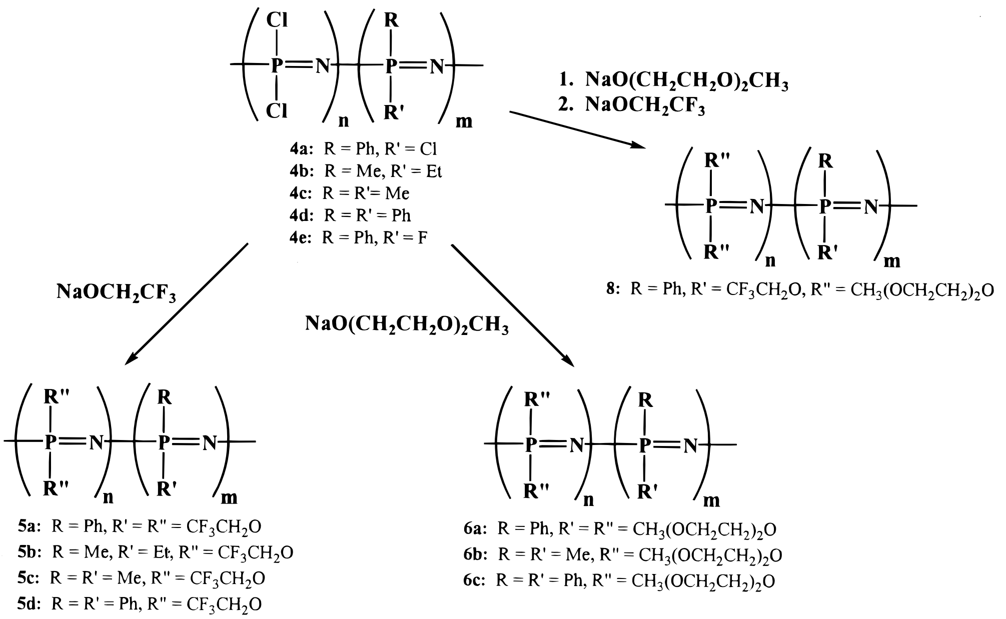


Table 3. Phosphazene Block Copolymer Data for $\{[N{=}P(OCH_2CH_2OCH_2CH_3)_2]_n[N{=}PR'(R')]_m\}$ Block Copolymers from $\{[N{=}PCl_2]_n[N{=}PR(R')]_m\}$ via Macromolecular Substitution with $NaO(CH_2CH_2O)_2CH_3$

			block copolymers M_w (10^{-4})			homopolymer[a] M_w (10^{-4})		
block copolymer	*n*:*m* (initial feed)	*n*:*m* (^{1}H NMR)	theor	actual (PDI)[a]	actual (PDI)[b]	theor	actual (PDI)[a]	yield[c] (%)
6a-1	**1** 0.51: **3a** 0.49	0.54:0.46	1.1	1.3 (1.07)	2.0(1.10)	0.58	0.81 (1.03)	86.4
6a-2	**1** 0.33: **3a** 0.67	0.42:0.58	1.5	1.9 (1.09)	2.6 (1.12)	0.57	0.80 (1.03)	84.8
6b	**1** 0.51: **3c** 0.49	0.54:0.46	0.99	1.3 (1.06)	2.1 (1.09)	0.79	0.71 (1.06)	73.4
6c	**1** 0.67: **3d** 0.33	0.72:0.28	0.75	1.0 (1.12)	1.8 (1.16)	0.55	0.79 (1.03)	73.0

[a] Molecular weights are based on polystyrene standards. [b] Molecular weights determined by light scattering. [c] Yields determined after dialysis with H_2O and MeOH (for 1 week each with 1000 MWCO tubing).

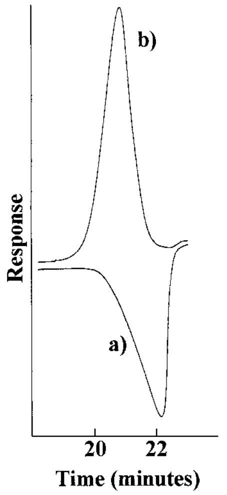


Figure 1. Comparison of GPC chromatograms from the polymerization of $Cl_3P{=}NSiMe_3$ (**2a**) initiated with PCl_5 in a 10:1 ratio: (a) after macromolecular substitution with $NaOCH_2CF_3$ to produce $[N{=}P(OCH_2CF_3)_2]_n$ (**2b**); (b) after addition of $PhCl_2P{=}NSiMe_3$ (**3a**) followed by macromolecular substitution with $NaOCH_2CF_3$ to produce $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**5a-1**). Note the increased molecular weight of the block copolymer and the reversal of the refractive index detector response.

polarity opposite to that of the trifluoroethoxy single-substituent polymer, $[N{=}P(OCH_2CF_3)_2]_n$ (Figure 1). The single-substituent control polymers **2b** were produced by removal of small aliquots of living **1** (formed by the polymerization of $Cl_3P{=}NSiMe_3$ (**2a**) with PCl_5) before the addition of a second phosphoranimine monomer. This polymer was then treated with sodium trifluoroethoxide. The detection of monomodal GPC peaks for the block copolymers, but with an opposite refractive index polarity from that of $[N{=}P(OCH_2CF_3)_2]_n$, indicates that block structures were present rather than two homopolymers. Similar changes in polarity have been reported for anionically produced phosphazene block copolymers.[12,13]

Methoxyethoxyethoxy (MEEP) Derivative Block Copolymers (6). Considerable interest exists in the synthesis of amphiphilic block copolymers with possible uses in membranes and surfactants. MEEP derivative block copolymers $\{[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N{=}PR(R')]_m\}$ (**6**) were synthesized via $\{[NPCl_2]_n[NPRR')_m]\}$ in order to incorporate both hydrophilic and hydrophobic properties into one copolymer. The hydrophilic segment consisted of a phosphazene with two methoxyethoxyethoxy substituents per phosphorus, while the other segment comprised either an aromatic side group plus a methoxyethoxyethoxy substituent, or two alkyl groups per phosphorus. In species **6a**, where one block contains both phenyl and methoxyethoxyethoxy side units, this block is amphiphilic while the second block is hydrophilic.

A route similar to the one used to prepare polymer **5** was employed to produce the MEEP derivative block copolymers, **6**, the only difference being in the choice of nucleophile for the halogen replacement reaction. Reactions of the organophosphoranimine monomers **3** with living **1** (from a 10:1 reaction of $Cl_3P{=}NSiMe_3$ with PCl_5), resulted in the formation of block copolymers **4a**, **4c**, and **4d** (Table 3). The polymers formed were then treated with $NaOCH_2CH_2OCH_2CH_2OCH_3$ to produce the MEEP-type derivative block copolymers, **6** (Scheme 4).

The formation of block copolymers **6** was confirmed by the following evidence. Small aliquots of the reaction mixture from $Cl_3P{=}NSiMe_3$ and PCl_5 were removed and treated with $NaOCH_2CH_2OCH_2CH_2OCH_3$ to produce the MEEP single-substituent polymer as a control. The GPC chromatograms of the block copolymers indicated higher molecular weights than those of the MEEP single-substituent polymer. Contrary to the situation for the trifluoroethoxy derivative block copolymers **5**, no change in refractive index polarity was observed. ^{31}P NMR spectroscopy indicated the presence of characteristic peaks for both block segments (Table 3). For block copolymer **6a**, peaks were present for $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ at −6.3 ppm and $[N{=}PPh(OCH_2CH_2OCH_2CH_2OCH_3)]_m$ at −0.5 ppm. The agreement between ^1H NMR integration and elemental analysis further supports the structure of these copolymers (see Experimental Section).

The $[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ single-substituent polymer (MEEP) is soluble in water whereas the phenyl−methoxyethoxyethoxy homopolymer, $[N{=}PPh(OCH_2CH_2OCH_2CH_2OCH_3)]_n$, is considerably less hydrophilic and is insoluble in water. Thus, in both the homo- and block copolymers, the hydrophobic aromatic groups and the hydrophilic methoxyethoxyethoxy groups together confer amphiphilic character to the macromolecules. Other polymers investigated contained blocks of the hydrophobic poly(diphenylphosphazene), $(N{=}PPh_2)_n$ together with the alkyl ether groups (**6c**). These polymers are insoluble in water. Poly(dimethylphosphazene) units, $(N{=}PMe_2)_n$ appear to be on the borderline between being hydrophilic or hydrophobic. The homopolymer is not soluble in water, but some combinations of hydrophobic and hydrophilic groups yielded polymers (**6b**) that are water-soluble. All are amphiphilic. These block copolymers are soluble in methanol and were purified by dialysis against water and methanol. However, the solubility of the block copolymers in water varied with the length of the second block and the precise side group structure.

NMR Analysis of $\{[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ (4b). ^{31}P NMR spectroscopy of the diblock copolymer **4b** revealed the presence of the characteristic resonances for $[N{=}PMe(Et)]_m$ at ca. 20 ppm and for $[N{=}PCl_2]_n$ at ca. −17 ppm. Also present in this spectrum were multiplet resonances at approximately 31.1, 28.1, −19.6, and −24.7 ppm, which could represent either polymer end groups or the switching groups that link the two phosphazene segments (Figure 2). To resolve this question, a model short chain phosphazene cation, $[Cl_3P{=}N{-}PCl_2{=}N{-}PMe(Et){=}N{-}PMe(Et)Cl]^+$ $[PCl_6]^-$ (**4b′**), was synthesized by successive additions of **3b** to $[Cl_3P{=}N{-}PCl_3]^+[PCl_6]^-$.[17] Analysis of **4b′** by ^{31}P NMR spectroscopy showed multiplet resonances at 27.1 and −14.1 ppm assigned to the junction groups $-PCl_2$ and $-PMe(Et)$, respectively. Thus, the broad multiplet peaks at 28.1 and −19.6 ppm of **4b** were assigned to the junction units.

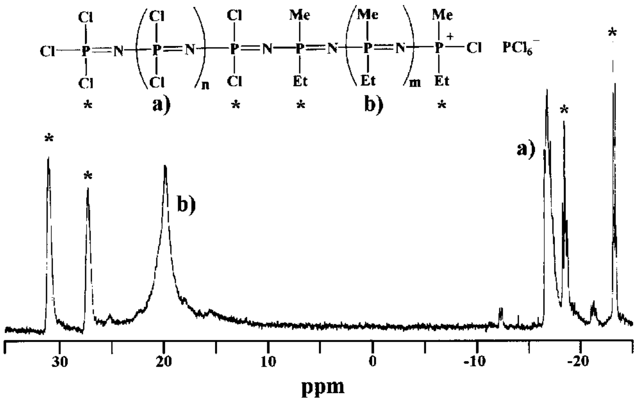
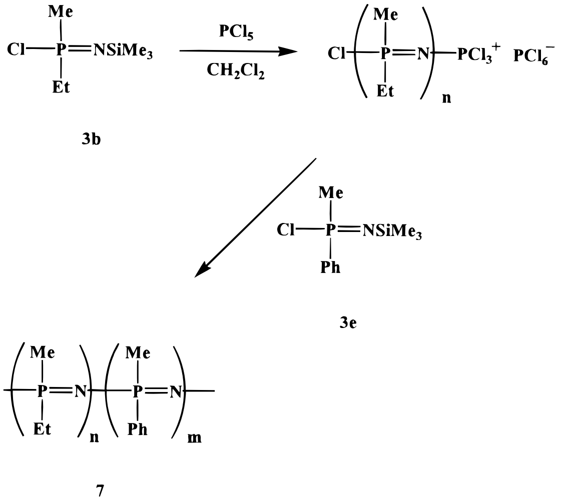


Figure 2. ^{31}P NMR spectrum of $\{[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ (**5b**). The peaks identified by stars have not yet been assigned to specific phosphorus atoms.

Scheme 5

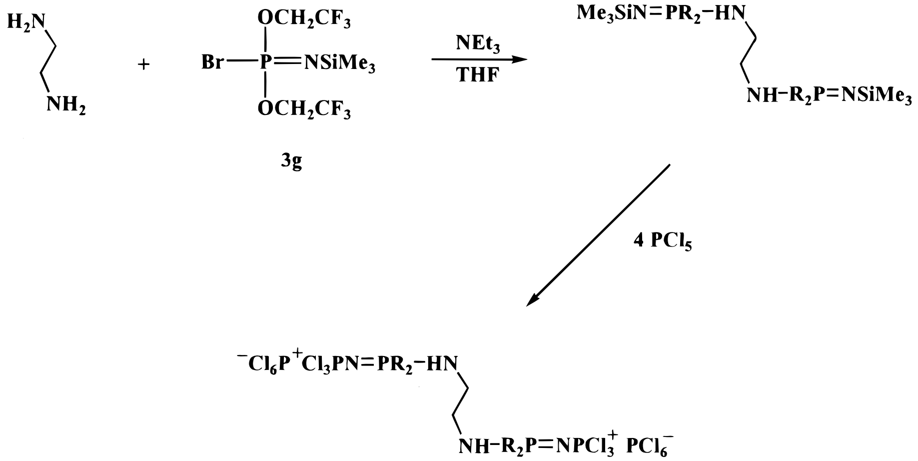


Phosphazene Block Copolymers from Two Different Organophosphoranimines. Organophosphoranimines can polymerize not only from living $(NPCl_2)_n$, but also from living poly(*organo*phosphazenes). The reaction sequence is shown in Scheme 5. For example, the polymerization of $Me(Et)ClP{=}NSiMe_3$ (**3b**) initiated by PCl_5 was accomplished in the solution-free state at 35 °C to form a living sample of the methyl−ethyl−polymer, $[Cl(PMe(Et){=}N)_nPCl_3]^+[PCl_6]^-$. Treatment of this species with $Me(Ph)ClP{=}NSiMe_3$ (**3f**) allowed the formation of the block copolymer $\{[N{=}PMe(Et)]_n[N{=}PMe(Ph)]_m\}$ (**7**) with $M_n = 1.4 \times 10^4$ and PDI = 1.18.

Mixed Chloro−Fluoro Diblock Copolymers. Alternative Route to $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (5a). The phosphoranimine $PhF_2P{=}NSiMe_3$ (**3e**)[25] reacted with living samples of **1**, to produce the mixed-halogeno block copolymer $\{[N{=}PCl_2]_n[N{=}PPh(F)]_m\}$ (**4e**). The ^{31}P NMR spectrum of this polymer contains a singlet at −17 ppm which is characteristic of $(NPCl_2)_n$, together with a broad doublet at ca. 10.4−3.7 ppm ($^2J_{P-F}$ = 972 Hz), which is indicative of the $[N{=}PPh(F)]_m$ segment. Subsequent treatment of this reaction mixture with $NaOCH_2CF_3$ in refluxing dioxane replaced all the chlorine *and* fluorine atoms by trifluoroethoxy groups. GPC analysis of this macromolecule revealed $M_n = 4.5 \times 10^4$ (PDI = 1.30). ^{31}P NMR spectroscopy indicated the presence of characteristic peaks for both $[N{=}PPh(OCH_2CF_3)]_m$ at 3.1 ppm and $[N{=}P(OCH_2CF_3)_2]_n$ at −6.9 ppm, which integrated in a 0.55:0.45 ratio. These results indicate that the block copolymer $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ **5a** had been formed. Thus, block copolymer **5a** is accessible through the copolymerization of either monomer **3e** or **3a**.

Selective Halogen Replacement. Phosphorus−fluorine and phosphorus−chloride bonds have different

Scheme 6



reactivities toward nucleophiles.[26,27] These differences can be utilized for the controlled or regioselective incorporation of different side groups. This was accomplished through the controlled incorporation of two different side groups in the block copolymer $\{[N{=}PCl_2]_n\text{-}[N{=}PPh(F)]_m\}$ (**4e**) by the sequential addition of two different nucleophiles. A sample of the mixed chloro−fluoro block copolymer **4e** was first treated with sodium methoxyethoxyethoxide (1 equiv per chlorine atom) at room temperature in THF. Examination of the reaction mixture by ^{31}P NMR spectroscopy showed that all the chlorine atoms in copolymer **4e** had been replaced to give $\{[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2\,]_n[N{=}PPh(F)]_m\}$, but that the fluorine atoms were still present. The peak at −17 ppm, attributed to the $(NPCl_2)_n$ segment, was shifted to −6.3 ppm, while the broad doublet characteristic of the $[N{=}PPh(F)]_m$ segment remained unchanged. Sodium trifluoroethoxide (1.1 equiv per fluorine atom) was then added to this copolymer in refluxing THF to replace the fluorine atoms in the $[N{=}PPh(F)]_m$ units and yield $\{[N{=}P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**8**). Analysis of **8** by multinuclear NMR and elemental analysis confirmed the proposed structure, and GPC analysis indicated that this polymer had an $M_n = 4.8 \times 10^4$ and PDI = 1.29. This confirmed that different nucleophiles can be selectively incorporated into these mixed halogen copolymers.

Although we have not yet examined this possibility, utilization of the cleaner replacement of fluorine than chlorine by organometallic reagents (such as Grignard or organolithium species)[27] opens up additional avenues for the control of polymer structure for these block copolymers.

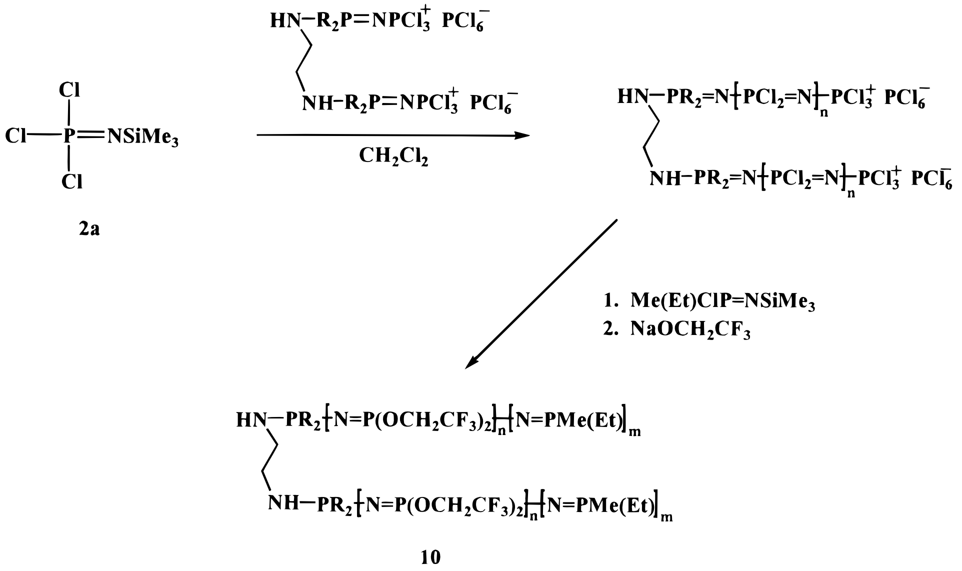
Phosphazene Triblock Copolymers. Recent extensions of the ambient temperature polymerization method in our laboratory have yielded triarmed star-branched polyphosphazenes via the reaction of $Cl_3P{=}NSiMe_3$ (**2a**) with a small amount of a trifunctional cationic species.[20] In that work, the multifunctional initiator was synthesized by reaction of the tridentate primary amine $N(CH_2CH_2NH_2)_3$ with $(CF_3CH_2O)_2BrP{=}NSiMe_3$ (**3g**), in the presence of NEt_3, to produce the trifunctional phosphoranimine $N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}NSiMe_3\}_3$, and subsequent reaction with six molar equivalents of PCl_5 at −78 °C in CH_2Cl_2 resulted in the formation of the trifunctional initiator $[N\{CH_2CH_2NH(CF_3CH_2O)_2P{=}N{-}PCl_3^+\}_3][PCl_6^-]_3$. Given these findings, attempts were made in this present work to synthesize linear difunctional initiators via the reactions of commercially available diamines, such as $NH_2CH_2CH_2NH_2$, to produce phosphazene multiblock copolymers.

Ethylenediamine was treated with $(CF_3CH_2O)_2BrP{=}NSiMe_3$ (**3g**) in the presence of triethylamine to produce the phosphoranimine $-(CH_2NH(CF_3CH_2O)_2P{=}NSiMe_3)_2$. Subsequent reaction of this species with 4 molar equiv of PCl_5 at −78 °C in CH_2Cl_2 yielded the difunctional initiator $-[CH_2NH(CF_3CH_2O)_2P{=}NPCl_3^+]_2[PCl_6^-]_2$ (Scheme 6). The addition of a 40-fold excess of $Cl_3P{=}NSiMe_3$ (**2a**) to the initiator at 25 °C then brought about the complete conversion of **2a** to a new form of poly(dichlorophosphazene), $-\{CH_2NH(CF_3CH_2O)_2P{-}[N{=}PCl_2]_nN{-}PCl_3^+PCl_6^-\}_2$. This was confirmed by the presence in the ^{31}P NMR spectrum of a resonance at −17 ppm, while the doublet resonances for $-[CH_2NH(CF_3CH_2O)_2P{=}NPCl_3^+]_2[PCl_6^-]_2$ had disappeared. The addition of $Me(Et)ClP{=}NSiMe_3$ (**3b**) in CH_2Cl_2 at 35 °C to this unterminated sample of poly(dichlorophosphazene) resulted in the formation of the phosphazene triblock copolymer $\{[(Et)MeP{=}N]_m[Cl_2P{=}N]_n\text{-}P(OCH_2CF_3)_2{-}NHCH_2CH_2NH{-}(CF_3CH_2O)_2P{-}[N{=}PCl_2]_n[N{=}PMe(Et)]_m\}$ (**9**). Examination of polymer **9** by ^{31}P NMR spectroscopy showed the presence of resonances characteristic for $[N{=}PMe(Et)]_m$ at approximately 20 ppm and for $[N{=}PCl_2]_n$ at about −17 ppm. Chlorine replacement by $NaOCH_2CF_3$ in refluxing dioxane yielded the hydrolytically stable triblock copolymer $\{[(Et)MeP{=}N]_m\text{-}[(CF_3CH_2O)_2P{=}N]_n{-}P(OCH_2CF_3)_2{-}NHCH_2CH_2NH{-}(CF_3CH_2O)_2P{-}[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe(Et)]_m\}$ (**10**) with $M_n = 2.1 \times 10^4$ (PDI = 1.21) (Scheme 7). The refractive index of the GPC peak for the triblock copolymer **10** was found to be of opposite polarity to that normal for the bis(trifluoroethoxy) single-substituent polymer **2b**. Further evidence for the structure of **10** was provided by comparison of the ^1H and ^{31}P NMR integration for the respective blocks ($n{:}m = 0.49{:}0.51$) with the elemental microanalysis results, which agree within experimental error (see Experimental Section).

Summary

The synthesis of phosphazene di- and triblock copolymers has been accomplished via the controlled, cationic ambient temperature polymerization of phosphoranimines. This method has been shown to be applicable to a wide range of phosphoranimines. Narrow molecular weight distributions have also been obtained. The architectures and properties of these block copolymers

Scheme 7



are tailored by the choice of phosphoranimine monomer, the selection of nucleophile for macromolecular substitution, the different reactivities of P−Cl and P−F bonds, and the use of mono- and difunctional initiators. The formation of hydrophobic/hydrophilic phosphazene block copolymers is significant from a fundamental perspective, as well as for practical applications in composites, membranes, and other materials. Some of the copolymers with poly[bis(trifluoroethoxy)phosphazene] blocks were opalescent, and this was taken as evidence for phase separation. Both wide angle x-ray diffraction and thermal analysis agree with this interpretation. A detailed examination of the properties of the block copolymers will be described in forthcoming publications. Current work is also being directed toward the synthesis of higher molecular weight polyphosphazenes by this method and the preparation of polymers with both organic and phosphazene blocks.

Experimental Section

Materials. Sodium trifluoroethoxide ($NaOCH_2CF_3$),[16] $[Cl_3P{=}NPCl_3]^+[PCl_6]^-$,[28] and the phosphoranimines $Cl_3P{=}NSiMe_3$ (**2a**),[15,28] $PhCl_2P{=}NSiMe_3$ (**3a**),[17,28] $Me(Et)ClP{=}NSiMe_3$ (**3b**),[17] $Me_2ClP{=}NSiMe_3$ (**3c**),[6,7,19] $Ph_2ClP{=}NSiMe_3$ (**3d**),[17] $Ph(Me)ClP{=}NSiMe_3$ (**3f**),[7] $PhF_2P{=}NSiMe_3$ (**3e**),[24,25] and $BrP(OCH_2CF_3)_2{=}NSiMe_3$ (**3g**)[20] were synthesized via methods reported previously.

Equipment. Glassware was dried overnight in an oven or flame-dried under vacuum before use. All reaction mixtures were protected under an atmosphere of dry argon or nitrogen. ^{31}P, ^{13}C, and ^{1}H NMR spectra were recorded with a Bruker WM-360 NMR spectrometer operated at 146, 90.27, and 360 MHz, respectively. ^{1}H and ^{13}C NMR spectra are referenced to internal $CDCl_3$ or $CD_3C(O)CD_3$. ^{31}P NMR chemical shifts are relative to 85% phosphoric acid as an external reference, with positive shift values downfield from the reference. Molecular weights were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector and American Polymer Standards AM gel 10 mm and Am gel 10 mm 10^4 Å columns, which were calibrated vs polystyrene standards (Polysciences). Absolute molecular weights were determined by GPC-MALLS using a Hewlett-Packard HP 1100 gel permeation chromatograph equipped with an Optilab DSP interferometric detector and Dawn DSP laser photometer operated at 488 nm (Wyatt Technology). The GPC samples were eluted with 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). The d*n*/d*c* values were determined individually for each block copolymer analyzed. Therefore, the M_w values are absolute rather than estimates.Elemental analyses were obtained by Quantitative Technologies Inc., Whitehorse, NJ.

Synthesis of $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (5a). (a) The room-temperature polymerizations were conducted in the following manner: To a stirred solution of PCl_5 (ca. 0.19 g, 0.91 mmol) in 20 mL of CH_2Cl_2 was added **2a** (2.00 g, 8.95 mmol), and the resultant reaction mixture was stirred at 25 °C. After complete conversion of **2a** to living poly(dichlorophosphazene) (**1**), as determined by ^{31}P NMR spectroscopy (ca. 3 h for $[N{=}PCl_2]_n$; ^{31}P NMR (CH_2Cl_2) $\delta = -17.4$ ppm), half of the reaction mixture was treated with $NaOCH_2CF_3$ to produce the trifluoroethoxy derivative $[N{=}P(OCH_2CF_3)_2]_n$ (**2b**). GPC data for **2b**: $M_n = 9.6 \times 10^3$ and PDI = 1.11. To the remainder of the reaction solution was added 4.72 g (17.8 mmol) of $PhCl_2P{=}NSiMe_3$ (**3a**) (in a 4:1 ratio with respect to **2a**) and the resultant mixture was stirred for 1 week with occasional monitoring by ^{31}P NMR spectroscopy. After complete conversion of **3a** to polymer, all volatiles were removed at reduced pressure. Treatment of the resultant $\{[N{=}PCl_2]_n[N{=}PPh(Cl)]_m\}$ (**4a**) with $NaOCH_2CF_3$ in dioxane produced $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PPh(OCH_2CF_3)]_m\}$ (**5a-1**). The polymer was purified by precipitatations from THF into deionized water (3×) and hexanes (2×). GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.13. ^{31}P NMR (CH_2Cl_2): $\delta = 3.1$ (s, $[N{=}PPh(OCH_2CF_3)]_m$), −6.9 ppm (s, $[N{=}P(OCH_2CF_3)_2]_n$). Anal. Calcd: C, 37.75; H, 2.82; N, 6.20. Found: C, 37.48; H, 2.75; N, 5.89. (b) For the modified polymerization, the above procedure was again followed; however, upon addition of **3a**, the reaction mixture was heated to 35 °C with stirring to remove volatiles by evaporation. See Tables 1−3 for characterization data of the block copolymers **5a-2**, **5a-3**, **5a-4**, and **5a-5**.

Synthesis of $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe(Et)]_m\}$ (5b). The synthesis of **5b** was performed in a manner similar to the preparation of copolymer **5a**. A control living sample of **1** was treated with $NaOCH_2CF_3$ to produce **2b**. GPC data for **2b**: $M_n = 1.3 \times 10^4$ and PDI = 1.06. Addition of $Me(Et)ClP{=}NSiMe_3$ (**3b**) (in a 2:1 ratio with respect to **2a**) to the remaining **1** and subsequent reaction with $NaOCH_2CF_3$ yielded **5b**. ^{31}P NMR (CH_2Cl_2): $\delta = 20.0$ (s, $[N{=}PMe(Et)]_m$), −6.9 ppm (s, $[N{=}P(OCH_2CF_3)_2]_n$). GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.19. Anal. Calcd: C, 28.02; H, 4.62; N 9.74. Found: C, 27.19; H, 5.09; N, 8.80.

Synthesis of $\{[N{=}P(OCH_2CF_3)_2]_n[N{=}PMe_2]_m\}$ (5c). The synthesis of **5c** was also carried out in a manner similar to the preparation of copolymer **5a**. A living sample of **1** was treated with $NaOCH_2CF_3$ to produce **2b** as a control. GPC data for **2b**: $M_n = 1.3 \times 10^4$ and PDI = 1.04. Addition of $Me_2ClP{=}NSiMe_3$ (**3c**) (in a 1:1 ratio with respect to **2a**) to the remaining

1 and subsequent reaction with $NaOCH_2CF_3$ resulted in **5c**. ^{31}P NMR (CH_2Cl_2): $\delta = 7.1$ (br s, $[N=PMe_2]_m$), -6.9 ppm (s, $[N=P(OCH_2CF_3)_2]_n$). GPC: $M_n = 1.6 \times 10^4$ and PDI = 1.14. Anal. Calcd: C, 21.7; H, 2.7; N, 7.8. Found: C, 22.29; H, 2.76; N, 7.52.

Synthesis of $\{N=P(OCH_2CF_3)_2]_n[N=PPh_2]_m\}$ (5d). The synthesis of **5d** was also carried out following the general procedure described for **5a**. A control living sample of $(N=PCl_2)_n$ (**1**) was treated with $NaOCH_2CF_3$ to produce **2b**. GPC data for **2b**: $M_n = 1.9 \times 10^4$ and PDI = 1.05. Addition of $Ph_2ClP=NSiMe_3$ (**3d**) (in a 1:2 ratio with respect to **2a**) to the remaining **1** and subsequent reaction with $NaOCH_2CF_3$ resulted in **5d**. ^{31}P NMR (CH_2Cl_2): $\delta = -6.5$ ppm (br s, $[N=PPh_2]_m$), -6.9 ppm (s, $[N=P(OCH_2CF_3)_2]_n$). GPC: $M_n = 2.0 \times 10^4$ and PDI = 1.25. Anal. Calcd: C, 29.6; H, 2.3; N, 6.0. Found: C, 32.94; H, 2.46; N, 5.88.

Synthesis of $\{[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n-[N=PPh(OCH_2CH_2OCH_2CH_2OCH_3)_2]_m\}$ (6a). The synthesis of **6a** was also carried out using the method described for **5a**. However, a living sample of **1** was treated with $NaOCH_2CH_2OCH_2CH_2OCH_3$ to produce $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$. Addition of $PhCl_2P=NSiMe_3$ (**3c**) to the remaining $(N=PCl_2)_n$ and subsequent reaction with $NaOCH_2CH_2OCH_2CH_2OCH_3$ resulted in **6a**. ^{31}P NMR (CH_2Cl_2): $\delta = -0.5$ ppm (br s, $[N=PPh(OCH_2CH_2OCH_2CH_2OCH_3)]_m$), -6.3 ppm (s, $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$). GPC: See Table 3. Anal. (for **6a-1** from 1:1 ratio of **3c** to **2a**) Calcd: C, 47.6; H, 10.6; N, 5.3. Found: C, 46.48; H, 6.93; N, 5.11.

Synthesis of $\{[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N=PMe_2]_m\}$ (6b). The synthesis of **6b** followed the procedure described for **6a**. A living sample of $(N=PCl_2)_n$ (**1**) was treated with $NaOCH_2CH_2OCH_2CH_2OCH_3$ to produce $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$. GPC data for $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$: $M_n = 6.7 \times 10^4$ and PDI = 1.06. Addition of $Me_2ClP=NSiMe_3$ (**3c**) (in a 1:1 ratio with respect to **2a**) to the remaining **1** and subsequent reaction with $NaOCH_2CH_2OCH_2CH_2OCH_3$ resulted in **6b**. ^{31}P NMR (CH_2Cl_2): $\delta = 7.1$ ppm (br s, $[N=PMe_2]_m$), -6.3 ppm (s, $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$). GPC: $M_n = 1.2 \times 10^4$ and PDI = 1.06. Anal. Calcd: C, 40.5; H, 7.9; N, 7.5. Found: C, 38.87; H, 7.20; N, 6.87.

Synthesis of $\{[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N=PPh_2]_m\}$ (6c). The synthesis of **6c** followed the same procedure as described for **6a**. A living sample of **1** was treated with $NaOCH_2CH_2OCH_2CH_2OCH_3$ to produce $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$ as a control. For $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$. GPC: $M_n = 7.7 \times 10^3$ and PDI = 1.03. Addition of $Ph_2ClP=NSiMe_3$ (**3d**) (in a 1:2 ratio with respect to **2a**) to the remaining **1** and subsequent reaction with $NaOCH_2CH_2OCH_2CH_2OCH_3$ resulted in **6c**. ^{31}P NMR (CH_2Cl_2): $\delta = -3.5$ ppm (br s, $[N=PPh_2]_m$), -6.3 ppm (s, $[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n$). GPC: $M_n = 8.9 \times 10^3$ and PDI = 1.12. Anal. Calcd: C, 47.8; H, 7.3; N, 5.3. Found: C, 47.95; H, 6.72; N, 5.67.

Alternative Synthesis of $\{[N=P(OCH_2CF_3)_2]_n[N=PPh(OCH_2CF_3)]_m\}$ (5a). The phosphazene block copolymer $\{[N=P(OCH_2CF_3)_2]_n[N=PPh(OCH_2CF_3)]_m\}$ (**5a**) was synthesized using previously reported methods that involved the addition of the fluorophosphoranimine $PhF_2P=NSiMe_3$ (**3e**) (in a 1:1 ratio with respect to **2a**) to living samples of $(N=PCl_2)_n$ (**1**) to form $\{[N=PCl_2]_n[N=PPh(F)]_m\}$ (**4e**), followed by treatment with $NaOCH_2CF_3$ (yield: 75.6%). GPC: $M_n = 4.5 \times 10^4$ and PDI = 1.30. ^{31}P NMR (CH_2Cl_2): $\delta = 3.1$ (s, $[N=PPh(OCH_2CF_3)]_m$), -6.9 ppm (s, $[N=P(OCH_2CF_3)_2]_n$).

Regiospecific Macromolecular Substitution of $\{[N=PCl_2]_n[N=PPh(F)]_m\}$ (4e). The partially fluorinated phosphazene block copolymer **4e** was dissolved in THF (100 mL) at room temperature and was treated with 1.0 M sodium methoxyethoxyethoxide (3.8 mmol) in THF (3.8 mL). The mixture was then stirred for 4 h. ^{31}P NMR spectroscopic analysis of the reaction mixture showed a broad peak at -6.3 ppm consistent with the formation of $\{[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n[N=PPh(F)]_m\}$. To this solution was then added 2.5 M sodium trifluoroethoxide (4.0 mmol) in dioxane (1.6 mL) and the mixture was stirred at reflux for 24 h to produce the macromolecule $\{[N=P(OCH_2CH_2OCH_2CH_2OCH_3)_2]_n-[N=PPh(OCH_2CF_3)]_m\}$ (**7**). Dialysis of this polymer in THF/water mixtures for 4 days produced **7** as a slightly yellow viscous oil. Yield: 78.0%. GPC: $M_n = 4.8 \times 10^4$ and PDI = 1.29. ^{31}P NMR (CH_2Cl_2): $\delta = 3.1$ (s, $[N=PPh(OCH_2CF_3)]_m$), -6.3 ppm (s, $[N=P(OCH_2CH_2OCH_2CH_2OCH_2)_2]_n$).

Synthesis of $[Cl_3P=N-PCl_2=N-PMe(Et)=N-PMe(Et)-Cl^+][PCl_6^-]$ (4b′). To a stirred solution of $[Cl_3P=NPCl_3]^+[PCl_6]^-$ (0.49 g, 0.91 mmol) in 1 mL of CH_2Cl_2 at -78 °C was added successive equivalents of **3b** (0.18 g, 0.91 mmol) in 1 mL of CH_2Cl_2, allowing each equivalent to react over a 1 h period before subsequent additions. After warming the solution to room temperature, all volatiles were removed under vacuum and the resultant oil $[Cl_3P=N-PCl_2=NPMe(Et)=NPMe(Et)-Cl^+][PCl_6^-]$ (**4b′**) was washed with hexanes and dried in vacuo. Yield: 0.57 g (90%). ^{31}P NMR (CD_2Cl_2): $\delta = 55.1$ (d, $^2J_{PP} = 40$ Hz, $-N=PMe(Et)Cl$), 27.1 (m, $^2J_{PP} = 39$ Hz, $-N-PMe(Et)=$), -14.1 (m, $^2J_{PP} = 43$ Hz, $-N-PCl_2=$), -24.9 (d, $^2J_{PP} = 43$ Hz, $-N=PCl_3$), and -297 ppm (s, PCl_6^-). ^1H NMR (CD_2Cl_2): $\delta = 2.13$ (m, $^3J_{HP} = 12$ Hz, $-N=PCH_3(CH_2CH_3)$), 1.97 (m, $^3J_{HP} = 10$ Hz, $-N=PMe(CH_2CH_3)$), and 1.18 ppm (m, $^4J_{HP} = 3$ Hz, $-N=PMe(CH_2CH_3)$. ^{13}C NMR (CD_2Cl_2): $\delta = 30.1$ (m, $^2J_{CP} = 80$ Hz, $-N=PCH_3(CH_2CH_3)$), 21.9 (m, $^2J_{CP} = 80$ Hz, $-N=PCH_3(CH_2CH_3)$), and 6.8 ppm (d, $^2J_{CP} = 5$ Hz, $-N=PCH_3(CH_2CH_3)$).

Preparation of $-(CH_2NH(CF_3CH_2O)_2P=NSiMe_3)_2$ (11). A mixture of $(CF_3CH_2O)_2BrPNSiMe_3$ (**3g**) (16.0 g, 40.4 mmol) and NEt_3 (4.08 g, 40.4 mmol) in THF (200 mL) was cooled to -78 °C. To this solution $NH_2CH_2CH_2NH_2$ (1.21 g, 20.2 mmol) was added dropwise over 20 min. The reaction mixture was stirred at -78 °C for 1 h and then warmed to room temperature. All volatiles were removed in vacuo to produce an orange oil which was used without further purification. Yield 12.4 g (89.6%). ^1H NMR ($CDCl_3$): $\delta = 4.23$ (q, $^3J_{HF} = 16$ Hz, 4H, CF_3CH_2O), 2.95 (br m, $^2J_{HH} = 12$ Hz, 4H, $-CH_2-NH$), 1.05 (br s, 2H, $-NH$), 0.04 ppm (d, $^4J_{HP} = 1$ Hz, 9H, $-CH_3-Si$). ^{31}P NMR ($CDCl_3$): $\delta = -1.1$ ppm. ^{13}C NMR ($CDCl_3$): $\delta = 124.6$ (d of q, $^2J_{CF} = 310$ Hz, $^3J_{CP} = 9$ Hz, CF_3), 61.8 (d of q, $^2J_{CP} = 10$ Hz, $^3J_{CF} = 36$ Hz, CH_2O), 42.2 (s, $-CH_2-N$), 4.4 ppm (d, $^3J_{CP} = 1$ Hz, $Si-CH_3$).

Preparation of $-[CH_2NH(CF_3CH_2O)_2P=NPCl_3^+]_2-[PCl_6^-]_2$. To a stirred solution of PCl_5 (3.96 g, 19.0 mmol) in CH_2Cl_2 (200 mL) at -78 °C was added $-(CH_2NH(CF_3CH_2O)_2P=NSiMe_3)_2$ (3.25 g, 4.7 mmol) dropwise over a period of 20 min. The reaction mixture was stirred at -78 °C for 1 h and allowed to warm to room temperature. After solvent removal in vacuo, the remaining residue was washed with hexane (4 × 100 mL) to produce $-[CH_2NH(CF_3CH_2O)_2P=NPCl_3^+]_2[PCl_6^-]_2$ as a light yellow solid. Yield: 4.5 g (70%). ^{31}P NMR ($CDCl_3$): $\delta = 14.5$ (d, $^2J_{PP} = 51$ Hz, $(CF_3CH_2O)_2P=N)$), 5.5 (d, $^2J_{PP} = 51$ Hz, $-N-Cl_3P$) and -297 ppm (s, PCl_6^-).

Synthesis of $\{[(Et)MeP=N]_m[(CF_3CH_2O)_2P=N]_n-P(OCH_2CF_3)_2-NHCH_2CH_2NH-(CF_3CH_2O)_2P[N=P(OCH_2CF_3)_2]_n[N=PMe(Et)]_m\}$ (10). To a stirred solution of $-[CH_2NH(CF_3CH_2O)_2P=NPCl_3^+]_2$ $[PCl_6^-]_2$ (0.1 g, 0.1 mmol) in CH_2Cl_2 (10 mL) at 25 °C was added **2a** (0.97, 4.3 mmol). After 3 h, all of the initial monomer **2a** had reacted, as indicated by the disappearance of the ^{31}P NMR resonance for **2a** at -54 ppm and the presence of a new resonance at -17.6 ppm for $(N=PCl_2)_n$. Data for $-[CH_2NH(CF_3CH_2O)_2P=N-PCl_2=N-PCl_3^+ PCl_6^-]_2$: ^{31}P NMR (CH_2Cl_2) $\delta = 8.2$ (d, 1P, $^2J_{PP} = 29$ Hz, $(CF_3CH_2O)_2P=N-$), -14.5, -15.5 (t, 2P, $^2J_{PP} = 40$ Hz, $(CF_3CH_2O)_2P=N-PCl_2N=PCl_2(N=PCl_2)_n]$), -17.6 ppm (br s, P, $[N=PCl_2]_n$). A portion of the reaction mixture was removed and dried under vacuum. The residue was then dissolved in 10 mL of dioxane and treated with 2.5 M sodium trifluoroethoxide (10 mmol) in dioxane (4 mL). The mixture was refluxed for 1 h, and stirred at 25 °C for 24 h to produce the macromolecule $-[CH_2NH(CF_3CH_2O)_2P=N-P(OCH_2CF_3)_2-(N=P(OCH_2CF_3)_2)_n]_2$. The polymer was then precipitated into deionized water (3×) and hexane (2×). Data for $-[CH_2NH-(CF_3CH_2O)_2P=N-P(OCH_2CF_3)_2(N=P(OCH_2CF_3)_2)_n]_2$: ^{31}P NMR (CH_2Cl_2) $\delta = -6.9$ ppm; ^1H NMR ($CDCl_3$) $\delta = 4.23$ (q, $^3J_{HF} = 16$ Hz, 2H, $-CH_2O$), 3.05 (br m, $^2J_{HH} = 12$ Hz, 2H, $-CH_2-NH$), 2.5 (br t, $^2J_{HH} = 11$ Hz, 2H, $N-CH_2-$), 1.23 (br s, 1H, $-NH$), 0.03 ppm (d, $^4J_{HP} = 1$ Hz, 9H, $Si-CH_3$-); GPC $M_n = 1.2 \times 10^4$ and PDI = 1.03. To $-[CH_2NH(CF_3CH_2O)_2P=N-$

$PCl_2{=}N{-}PCl_3^+\ PCl_6^-\}_2$ was added $Me(Et)ClP{=}NSiMe_3$ (**3b**) (0.86 g, 4.3 mmmol) (in a 1:1 ratio with respect to **2a**). The reaction mixture was heated to 35 °C with stirring to remove volatiles to result in block copolymer **10**. The block copolymer was then precipitated into deionized water (3×) and hexane (2×). Yield: 90%. ^{31}P NMR (CH_2Cl_2): $\delta = 20.0$ (s, $[N{=}PMe(Et)]_m$), -6.9 ppm (s, $[N{=}P(OCH_2CF_3)_2]_n$). GPC: $M_n = 2.1 \times 10^4$ and PDI = 1.21. Anal. Calcd: C, 25.30; H, 3.61; N, 4.30. Found: C, 25.28;, H, 3.05; N, 4.04.

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