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Side Group Exchange in Poly(organophosphazenes) with Fluoroalkoxy Substituents

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ABSTRACT: Several poly(alkoxyphosphazenes) and poly(fluoroalkoxyphosphazenes) were synthesized and allowed to react with various organic nucleophiles. Reactions were carried out at room temperature (25 °C) and at 67 °C in tetrahydrofuran (THF) and were monitored by ^{31}P NMR spectroscopy. The possible use of single-substituent polymers as hydrolytically stable macromolecular intermediates for mixed-substituent polyphosphazene synthesis is discussed, and factors that influence side group replacement in poly(organophosphazenes) are examined. In addition, evidence for a random, irreversible S$_N$2-like mechanism of side group replacement is presented.

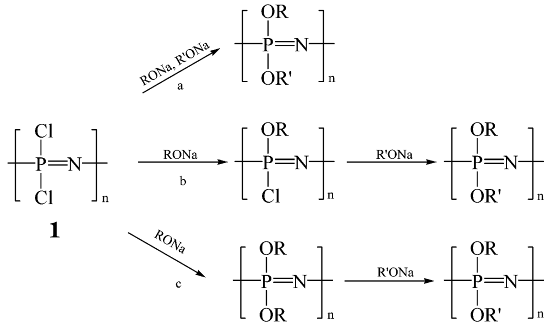
Introduction

Polyphosphazenes are inorganic backbone polymers that have a skeleton of alternating phosphorus and nitrogen atoms.[1] Two organic or organometallic side groups are linked to each phosphorus atom. These polymers are of interest as biomedical materials,[2,3] fire-retardants,[4,5] and low-temperature elastomers[6] and are under development as fuel cell membranes[7] and solid polymer lithium ion conductors.[8] A distinctive feature of polyphosphazenes is the ease with which polymer properties can be tuned through changes in the side groups linked to the phosphorus atoms.[9,10]

Several methods have been developed previously for the synthesis of poly(organophosphazenes). The most widely explored method is based on the ring-opening polymerization of hexachlorocyclotriphosphazene, $(NPCl_2)_3$, to poly(dichlorophosphazene), $(NPCl_2)_n$ (**1**), followed by the replacement of the labile chlorine atoms in this macromolecular intermediate by organic groups—typically alkoxy, aryloxy, or amino groups.[1,11,12] A second category of synthetic process involves the preparation of **1** by condensation methods, such as the thermal condensation of $OPCl_2{-}N{=}PCl_3$[13,14] and the living cationic polymerization of $Me_3Si{-}N{=}PCl_3$.[15,16] These various approaches provide access to several hundred different polymer systems, each with specific and often unique chemical and physical property combinations. In addition, several methods exist for the modification of these polymers by secondary reactions such as sulfonation,[17] lithiation,[18] hydrolysis,[19] etc.

An alternative method for structural modification involves the replacement of one organic side group linked to a phosphazene chain by another.[20] This is a secondary reaction that offers the prospect that single-substituent poly(organophosphazenes) can be converted readily to mixed-substituent species, especially for the preparation of mixed-substituent elastomers which are of broad technological interest. It also raises the possibility that an organophosphazene polymer that is stable for long periods of time in the atmosphere might be employed as a general macromolecular intermediate for the preparation of other poly(organophosphazenes). For some situations this would be an improvement over the use of **1** for this purpose because the chloro derivative is sensitive to moisture, must be stored under carefully controlled conditions, and can be used as a macromolecular intermediate only in a limited number of organic solvents.[5]

Scheme 1. Synthesis of Cosubstituted Poly(organophosphazenes): (a) Simultaneous Addition of Nucleophiles; (b) Sequential Addition of Nucleophiles; (c) Macromolecular Substitution of Poly(organophosphazene)



Cosubstituted poly(organophosphazenes) have traditionally been prepared through the sequential or simultaneous reaction of two or more nucleophiles with $(NPCl_2)_n$ (Scheme 1a,b). Alternatively, displacement of organic side groups on poly(organophosphazenes) by various nucleophiles would be an effective route to the same types of polymers (Scheme 1c).[20] Allcock, Kugel, and Walsh reported a series of side group exchange reactions between cyclic small molecule model organophosphazenes and organic nucleophiles.[21] Another study examined the exchange reactions of cyclophosphazene trimers that have phenoxy, chlorophenoxy, or nitrophenoxy side groups.[22] Although side group displacement was induced in these small molecule systems by nucleophiles such as 2,2,2-trifluoroethoxide, some side reactions also occurred. For example, α-carbon attack on the aryl group in the nitro-substituted rings has been detected, and ring degradation occurs in some cases.[22] In other work, *o*-nitrophenoxy groups were displaced from high polymeric poly[bis(*o*-nitrophenoxyphosphazene)] by sodium trifluoroethoxide. Although some side group displacement was detected, polymer degradation occurred again through α-carbon attack on the aryl group.[23]

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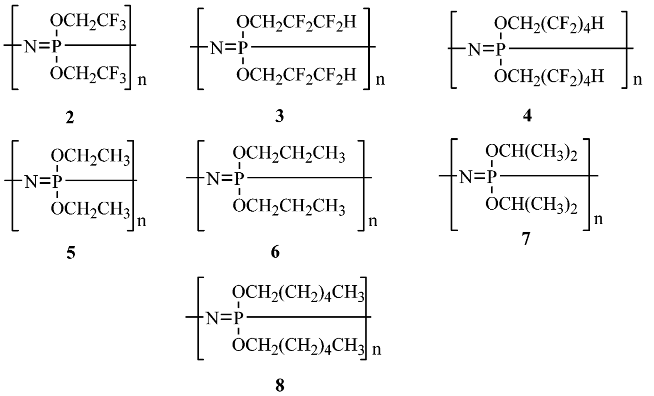


Figure 1. Starting polymers **2**−**8**.

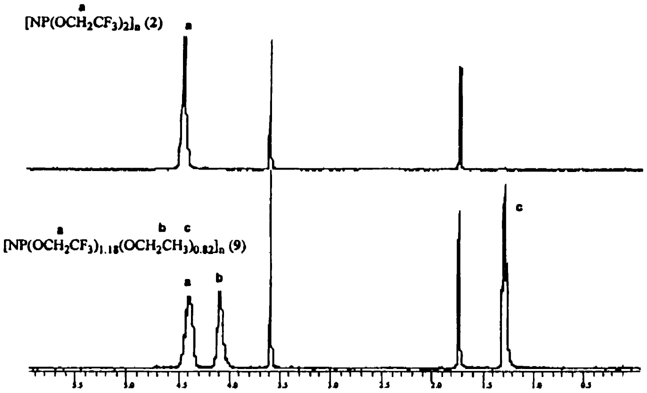


Figure 2. ^{1}H NMR spectra in d_8-THF.

Earlier preliminary work has shown that fluorinated alkoxy units[24] and phenoxy side groups can be displaced from polyphosphazenes.[20] The surface modification of poly[bis(trifluoroethoxy)phosphazene] (**2**) by displacement of trifluoroethoxy groups has also been studied.[25] For polyphosphazenes that bear both trifluoroethoxy and phenoxy side groups, replacement of phenoxy side groups by 2,2,2-trifluoroethoxide occurs only on nongeminally substituted phosphorus atoms. The reverse reaction, exchange of the trifluoroethoxy group by phenoxide ions, was not detected.[20]

In the present study, cosubstituted polyphosphazenes have been synthesized by macromolecular side group exchange reactions between poly[bis(fluoroalkoxy)phosphazenes] and several alkoxide nucleophiles. Stereoelectronic effects were investigated through varying both the reaction conditions and the type of nucleophile for each poly(organophosphazene).

Results and Discussion

Synthesis of Starting Macromolecules [NP(OR)$_2$]$_n$ (2−8). Poly(dichlorophosphazene) readily undergoes macromolecular replacement of the chlorine atoms to yield poly(organophosphazenes).[1,9] The course of these reactions can be followed by ^{31}P NMR spectroscopy. Fluoroalkoxy-substituted polymers **2**−**4** (Figure 1) were obtained via this route in good yields and at room temperature over 3−10 h reaction time. However, the preparation of nonfluorinated polymers **5** and **8** (Figure 1) required slightly elevated temperatures (~40 °C) for longer times (~18 h) to obtain complete substitution. Formation of polymer **6** (Figure 1) took place after heating for 36 h. The synthesis of polymer **7** (Figure 1) required heating to reflux for 48 h. The ease of macromolecular substitution can be affected by alkoxide solubility, but this low reactivity is probably due more to the steric bulk and lower nucleophilicity of the isopropoxide ion than to the low solubility of the nucleophile.

Reactions of [NP(OCH$_2$CF$_3$)$_2$]$_n$ (2) with Alkoxide Nucleophiles. Solutions of each of the fluoroalkoxy-substituted polymers (**2**−**4**) in THF were treated with solutions of sodium ethoxide, sodium propoxide, sodium isopropoxide, and sodium hexoxide at 25 °C and at the solvent reflux temperature (67 °C). These reactions were monitored using ^{31}P NMR spectroscopy. Although ^{31}P NMR chemical shifts change with side group replacement, the spectral changes could not be used to obtain quantitative information about the composition of the resultant polymers because of overlap of the phosphorus signals. Similarly, ^{19}F NMR spectra showed peak broadening with side group exchange, but these changes yielded little information that would allow monitoring of the side group ratios. However, ^{1}H NMR spectroscopy was utilized to ascertain the ratio of different side groups by integration of the proton signals from the α-carbon atoms of the alkoxy and fluoroalkoxy side groups (Figure 2).[26]

The results from the reaction of **2** with several different alkoxide nucleophiles at ambient temperature and at reflux are shown in Table 1. The highest degree of displacement at 25 °C was found for the formation of polymer **9**, where the ethoxide ion displaced 41% of the 2,2,2-trifluoroethoxy side groups. Reactions of polymer **2** with other nucleophiles at 25 °C gave less displacement, probably due to the larger size of the propoxide, isopropoxide, and hexoxide nucleophiles. The same trend was found for reactions at 67 °C, with sodium ethoxide displacing the largest percentage of 2,2,2-trifluoroethoxide groups, followed by sodium hexoxide and then the other alkoxides. The degree of substitution increased 15−20% with the 42 °C increase in reaction temperature. It might be expected, on the basis of steric hindrance considerations, that sodium propoxide would give more substitution than sodium hexoxide at 25 and 67 °C. However, this did not occur, possibly due to the lower solubility of sodium propoxide in THF. The similar side group ratios that were generated in polymers **11** and **13** and in **12** and **14** after reactions of polymer **2** with sodium propoxide and sodium isopropoxide suggest that the isopropoxide group is not seriously sterically hindered in its attack on the phosphorus atoms of **2**.

Reactions of [NP(OCH$_2$CF$_2$CF$_2$H)$_2$]$_n$ (3) with Alkoxide Nucleophiles. ^{1}H NMR spectroscopy was also used to determine the ratio of side groups present in cosubstituted polyphosphazenes **17**−**24**. The results followed similar trends to those found for polymer **2**, but fewer fluoroalkoxy side groups were displaced from polymer **3**. The highest degree of substitution was 33−36% for reaction with the ethoxide nucleophile at 67 °C (**18**) compared to 59−62% for **2** with the same nucleophile under the same conditions (**10**). Reactions of **3** in THF at 67 °C yielded an increase of only ~5−10% in the extent of substitution for reactions using the same nucleophiles at 25 °C. This is in contrast to increases of ~10−20% for reactions of polymer **2** carried out at 67 °C. The isopropoxide nucleophile displaced marginally fewer (4−5%) 2,2,3,3-tetrafluoropropoxide groups than the primary propoxide nucleophile. This is illustrated by a comparison of polymers **18** and **19** with polymers **20** and **21**. Thus, it appears that (surprisingly) the isopropoxide ion has roughly the same access to the

Table 1. Composition of Cosubstituted Polymers from 2 $[NP(OCH_2CF_3)_2]_n$

resultant polyphosphazene	reaction *T* (°C)	% substitution ^{1}H NMR	% substitution EA[a]
$[NP(OCH_2CF_3)_{1.18}(OCH_2CH_3)_{0.82})]_n$ (**9**)	25	41	44
$[NP(OCH_2CF_3)_{0.82}(OCH_2CH_3)_{1.18})]_n$ (**10**)	67	59	62
$[NP(OCH_2CF_3)_{1.48}(OCH_2CH_2CH_3)_{0.52}]_n$ (**11**)	25	26	29
$[NP(OCH_2CF_3)_{1.34}(OCH_2CH_2CH_3)_{0.66}]_n$ (**12**)	67	33	38
$[NP(OCH_2CF_3)_{1.52}(OCH(CH_3)_2)_{0.48})]_n$ (**13**)	25	24	27
$[NP(OCH_2CF_3)_{1.22}(OCH(CH_3)_2)_{0.78})]_n$ (**14**)	67	39	41
$[NP(OCH_2CF_3)_{1.42}(OCH_2(CH_2)_4CH_3)_{0.58}]_n$ (**15**)	25	29	33
$[NP(OCH_2CF_3)_{0.92}(OCH_2(CH_2)_4CH_3)_{1.08}]_n$ (**16**)	67	54	56

[a] Based on nitrogen-to-fluorine ratios from elemental analysis.

Table 2. Composition of Cosubstituted Polymers from 3 $[NP(OCH_2CF_2CF_2H)_2]_n$

resultant polyphosphazene	reaction *T* (°C)	% substitution ^{1}H NMR	% substitution EA[a]
$[NP(OCH_2CF_2CF_2H)_{1.18}(OCH_2CH_3)_{0.82})]_n$ (**17**)	25	25	27
$[NP(OCH_2CF_2CF_2H)_{0.82}(OCH_2CH_3)_{1.18})]_n$ (**18**)	67	33	36
$[NP(OCH_2CF_2CF_2H)_{1.48}(OCH_2CH_2CH_3)_{0.52}]_n$ (**19**)	25	19	23
$[NP(OCH_2CF_2CF_2H)_{1.34}(OCH_2CH_2CH_3)_{0.66}]_n$ (**20**)	67	23	27
$[NP(OCH_2CF_2CF_2H)_{1.52}(OCH(CH_3)_2)_{0.48})]_n$ (**21**)	25	14	17
$[NP(OCH_2CF_2CF_2H)_{1.22}(OCH(CH_3)_2)_{0.78})]_n$ (**22**)	67	19	24
$[NP(OCH_2CF_2CF_2H)_{1.42}(OCH_2(CH_2)_4CH_3)_{0.58}]_n$ (**23**)	25	20	26
$[NP(OCH_2CF_2CF_2H)_{0.92}(OCH_2(CH_2)_4CH_3)_{1.08}]_n$ (**24**)	67	30	34

[a] Based on nitrogen-to-fluorine ratios from elemental analysis.

backbone phosphorus atoms of polymer **3** as does the *n*-propoxide ion.

Reactions of $[NP(OCH_2(CF_2)_4H)_2]_n$ (4) with Alkoxide Nucleophiles. Similar trends were apparent for reactions of polymer **4** with the same four alkoxides as used with polymers **2** and **3**. Almost all of the cosubstituted polymers resulted from ~20% side group exchange after reactions at both 25 and 67 °C. The extent of displacement was ~5−10% less than for **3** and 20−30% less than the reactions of the same nucleophiles with **2**. Very little increase in the degree of displacement was detected with increased temperature for the reactions of **4**, especially with respect to the hexoxide substitutions that gave polymers **31** and **32** as compared to polymers **22** and **23**. The size of the 2,2,3,3,4,4,5,5-octafluoropentoxy side groups provides better shielding of the phosphorus atoms from nucleophilic attack, which leads to a decreased degree of displacement when compared with the displacement of 2,2,2-trifluoroethoxy or 2,2,3,3-tetrafluoropropoxy groups.

Reactions of 5−8 with Alkoxide Nucleophiles. No side group exchange was detected when poly[bis(ethoxy)phosphazene] (**5**), poly[bis(propoxy)phosphazene] (**6**), poly[bis(isopropoxy)phosphazene] (**7**), or poly[bis(hexoxy)phosphazene] (**8**) were treated with alkoxide nucleophiles. The nonfluorinated alkoxy groups are less electron withdrawing than the fluoroalkoxy units, and this renders the backbone phosphorus atoms less susceptible to nucleophilic attack than in the case of poly[bis(fluoroalkoxy)phosphazenes]. Thus, the electron-withdrawing ability of the initial side group appears to be a key factor that determines if side group displacement can occur. The degree of substitution is also affected by shielding of the backbone phosphorus as seen in the earlier work of Allcock and Kim[26] and confirmed by the current work.

Characterization of Polymers 2−32. ^{31}P NMR spectroscopy was used to monitor all the reactions. The side group replacement reactions were allowed to continue for 48 h, although no change in the phosphorus spectra was detected after 36 h for most of the polymers studied. The absence of peaks around 0 ppm indicated that no rearrangement of the polyphosphazene to a phosphazane had occurred. However, it is possible that substitution was accompanied by some chain cleavage because lower molecular weight polymers were detected from GPC plots of the cosubstituted polymers.

^{19}F NMR spectra were also obtained for each polymer. Peak broadening and unresolved splitting were present in each spectrum. No fluorine−fluorine coupling was detected in these polymers because the coupling constants are <1 Hz for vicinal fluoroalkyl species.[27]

Elemental analysis was used to confirm the composition of the polymers after side group displacement had occurred. The fluorine percentages obtained from this method were significantly lower than those calculated for each polymer. However, the differences between the calculated and found weight percentages for each of the other elements are minimal. It is known that high fluorine content can decrease the accuracy of fluorine elemental analysis.[28] Therefore, it is believed that elemental analyses, of the elements other than fluorine, adequately verifies the composition of our materials. Side group ratios based on the nitrogen-to-fluorine ratios from elemental analysis are included in Tables 1−3 for comparison.

The molecular weights of the starting polymers and the cosubstituted products were markedly different. Decreases in molecular weight were detected following the substitution reactions. Three explanations seem plausible. First, most of the introduced side groups have lower molecular weights than the fluorinated side groups displaced from the starting polymers. Second, the hydrodynamic radii of the resultant polymers could be very different from those of the starting polymers and this could affect elution from GPC columns.[29] Third, some chain cleavage could accompany macromolecular substitution reactions. For all the polymers except **14**, the first two explanations are preferred since there is little change in the shape of the peaks in the GPC traces. For polymer **14**, synthesized via reaction of the trifluoroethoxy single substituent polymer (**2**) with the isopropoxide nucleophile in refluxing THF, the GPC trace contained an unresolved bimodal peak indicative of chain cleavage. The isopropoxide ion is a stronger base than the other alkoxides and at reflux conditions could attack the backbone of polymer **2**. This is not observed for polymers **3** and **4** because the phosphorus−nitrogen

Table 3. Composition of Cosubstituted Polymers from 4 $[[NP(OCH_2CF_2CF_2\ CF_2CF_2H)_2]_n$

resultant polyphosphazene	reaction *T* (°C)	% substitution ^1H NMR	% substitution EA[a]
$[NP(OCH_2(CF_2)_4H)_{1.18}(OCH_2CH_3)_{0.82})]_n$ (**25**)	25	17	21
$[NP(OCH_2(CF_2)_4H)_{0.82}(OCH_2CH_3)_{1.18})]_n$ (**26**)	67	23	29
$[NP(OCH_2(CF_2)_4H)_{1.48}(OCH_2CH_2CH_3)_{0.52}]_n$ (**27**)	25	21	23
$[NP(OCH_2(CF_2)_4H)_{1.34}(OCH_2CH_2CH_3)_{0.66}]_n$ (**28**)	67	24	26
$[NP(OCH_2(CF_2)_4H)_{1.52}(OCH(CH_3)_2)_{0.48})]_n$ (**29**)	25	17	19
$[NP(OCH_2(CF_2)_4H)_{1.22}(OCH(CH_3)_2)_{0.78})]_n$ (**30**)	67	20	24
$[NP(OCH_2(CF_2)_4H)_{1.42}(OCH_2(CH_2)_4CH_3)_{0.58}]_n$ (**31**)	25	15	17
$[NP(OCH_2(CF_2)_4H)_{0.92}(OCH_2(CH_2)_4CH_3)_{1.08}]_n$ (**32**)	67	17	20

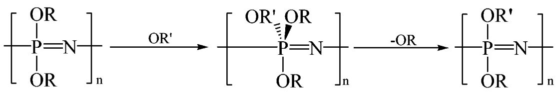
[a] Based on nitrogen-to-fluorine ratios from elemental analysis.

Table 4. GPC Results[a]

polymer	M_n	polymer	M_n	polymer	M_n
2	552 000	**13**	136 000	**24**	76 000
3	140 000	**14**	36 000	**25**	180 000
4	627 000	**15**	423 000	**26**	206 000
5	172 000	**16**	180 000	**27**	125 000
6	540 000	**17**	126 000	**28**	122 000
7	134 000	**18**	92 000	**29**	111 000
8	577 000	**19**	98 000	**30**	130 000
9	475 000	**20**	70 000	**31**	180 000
10	231 000	**21**	54 000	**32**	172 000
11	312 000	**22**	31 000		
12	202 000	**23**	97 000		

[a] Based on polystyrene standards.

Scheme 2. Addition/Elimination Mechanism of Macromolecular Substitution



backbone is better protected by the bulkier tetrafluoropropoxy and octafluoropentoxy side groups.

Factors Involved in Macromolecular Substitution of 2−4. As already noted, a key factor that determines whether side group displacement occurs in poly(organophosphazenes) is the electron-withdrawing ability of the initial side groups. Electron-withdrawing side groups make the phosphorus to which they are linked more susceptible to nucleophilic attack. However, the ability of the initial side groups to shield the backbone phosphorus atoms also plays an important role in determination of the degree of substitution.[20] Thus, while the 2,2,3,3-tetrafluoropropoxy and 2,2,3,3,4,4,5,5-octafluoropentoxy side groups are more electron-withdrawing than 2,2,2-trifluoroethoxy side group, they also shield the skeletal phosphorus atoms from nucleophilic attack to a greater degree. This results in a lower level of side group substitution.

Mechanism of Macromolecular Substitution. The reactions are believed to proceed via an S_N2-like addition−elimination reaction at the phosphorus atoms, as shown in Scheme 2. If the reaction proceeded in an S_N1-like fashion, the polymers with the more ionizable side groups, such as poly[bis(tetrafluoropropoxy)phosphazene] and poly[bis(octafluoropentoxy)phosphazene], would presumably be more prone to side group exchange than poly[bis(trifluoroethoxy)phosphazene].

Another question to consider is whether the mechanism consists of an equilibrium reaction of incoming and displaced nucleophiles or whether side group substitution is irreversible. To this end, polymers **9**, **10**, **15**, and **16** were exposed to 1 equiv/side group of sodium 2,2,2-trifluoroethoxide in THF for 48 h at 67 °C. No changes in the NMR spectra were detected, and this suggests the irreversibility of the side group displacement.

Multinuclear NMR spectroscopy provided evidence for a random disposition of side groups in the modified polymers. ^{31}P NMR spectra showed no evidence of sharp peaks that would be indicative of blocky structures but instead gave broad peaks. ^1H NMR spectra contained unresolved multiplets instead of sharp multiplets.

Conclusions

An alternative way to prepare cosubstituted poly[(fluoroalkoxy−alkoxy)phosphazenes] through side group exchange has been investigated. The degree of displacement of organic side groups in the poly[bis(alkoxy)phosphazene] system depends on both the electron-withdrawing ability of the side groups and the ability of the side group to protect the backbone phosphorus atoms from nucleophilic attack. The highest degree of replacement of side groups was ~60%. Thus, none of the polymers examined here could be completely converted to derivative single-substituent polymers in one reaction.

Although none of the starting polymers were found to be universal macromolecular intermediates with the broad versatility of **1**, the information obtained here is valuable for the synthesis of many cosubstituted polyphosphazenes. For example, it can be used to determine the order in which nucleophiles should be added to **1** to obtain specific side group ratios without side group exchange taking place during macromolecular substitution. It is also important for designing new high-performance elastomers with properties that differ from those of the existing fluoroalkoxyphophazene commercial materials.

Experimental Section

Materials. Ethanol, 1-propanol, 2-propanol, 1-hexanol, 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, and 2,2,3,3,4,4,5,5-octafluoropentanol from Aldrich were dried over CaH_2 and distilled before use. Sodium hydride (60% in mineral oil) was obtained from Aldrich and was weighed into Schlenk flasks in an argon-filled glovebox. Poly(dichlorophosphazene) (**1**) was prepared via thermal ring-opened polymerization as reported previously.[1] Tetrahydrofuran was distilled from sodium benzophenone ketyl under a dry argon atmosphere.

All glassware was flame-dried under vacuum or dried overnight in an oven before use. The reactions were carried out using standard Schlenk techniques under an atmosphere of dry argon.

Equipment. ^1H and ^{31}P spectra were recorded on a Bruker AMX-360 NMR spectrometer operated at 360 and 90.27 MHz, respectively. ^1H NMR spectra were referenced to external tetramethylsilane. ^{31}P and ^{19}F NMR (Bruker DPX-300, 282 MHz) proton-decoupled chemical shifts were relative to external 85% phosphoric acid standard and trichlorofluoromethane, respectively. Molecular weights and polydispersities were estimated using a Hewlett-Packard HP 1090 gel permeation chromatograph equipped with an HP-1047A refractive index detector, Phenomenex Phenogel 10 μm linear columns, and calibrated vs polystyrene standards. Sample elution was carried out at 40 °C with a 0.1 wt % solution of tetra-*n*-butylammonium nitrate (Aldrich) in THF (OmniSolv). Elemental analyses were obtained from Quantitative Technologies of Whitehouse, NJ.

Synthesis of Poly[bis(fluoroalkoxyphosphazenes)] [NP(OR)$_2$]$_n$ (2−4). Sodium fluoroalkoxide solutions were prepared via addition of 2,2,2-trifluoroethanol, 2,2,3,3-tetrafluoropropanol, or 2,2,3,3,4,4,5,5-octafluoropentanol (345 mmol) to a slurry of sodium hydride (60%) (13.4 g, 335 mmol) in THF (1.5 L) with cooling by an ice bath. Solutions of **1** (15.0 g, 129 mmol) dissolved in freshly distilled THF (1.5 L) were added dropwise to stirred solutions of the sodium fluoroalkoxide (335 mmol) in THF (1.5 L) at room temperature for 3−5 h. The reaction mixtures were concentrated by rotary evaporation, and polymers **2**−**4** were purified by multiple precipitations into acidified water (pH ∼ 5) and hexanes followed by drying on a vacuum line.

For **2:** white, semicrystalline material. Yield = 27.3 g (87%). ^{1}H NMR (d_8-THF): $\delta = 4.5$ (q, $J = 7.9$ Hz, 4H, OCH_2CF$_3$). ^{31}P NMR (d_8-THF): $\delta = -6.3$ (s). ^{19}F NMR (d_8-THF): −76.7 (s). Elemental analysis (calcd, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37), F = (46.91, 44.98).

For **3:** white, semicrystalline material. Yield = 31.7 g (80%). ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, OCH$_2$CF$_2$CF$_2$$H$), 4.4 (t, $J = 12.9$ Hz, 4H, OCH_2CF$_2$CF$_2$H). ^{31}P NMR (d_8-THF): $\delta = -6.8$ (s). ^{19}F NMR (d_8-THF): −128.2 (s), −141.4 (s). Elemental analysis (calcd, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37), F = (49.49, 48.24).

For **4:** white, waxlike material. Yield = 31.7 g (80%). ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t of t, $J = 52.5$, 25.2 Hz, 2H, OCH$_2$CF$_2$CF$_2$CF$_2$CF$_2$$H$), 4.3 (t, $J = 13.7$ Hz, 4H, OCH_2CF$_2$CF$_2$CF$_2$CF$_2$H). ^{31}P NMR (d_8-THF): $\delta = -5.8$ (s). ^{19}F NMR (d_8-THF): −122.3 (s), −126.4 (s), −131.1 (s), −139.5 (s). Elemental analysis (calcd, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37), F = (59.96, 59.34).

Synthesis of Poly[bis(alkoxyphosphazenes)] [NP(OR)$_2$] (5−8). Sodium alkoxide solutions were prepared via the addition of ethanol, 1-propanol, 2-propanol, or 1-hexanol (345 mmol) to a slurry of NaH (60%) (13.4 g, 335 mmol) in THF (1.5 L) with stirring. Heat was applied to ensure conversion to the sodium salt. Solutions of **1** (15.0 g, 129 mmol) dissolved in freshly distilled THF (1.5 L) were added dropwise to stirred solutions of the sodium alkoxide (335 mmol) in THF (1.5 L) at ∼50 °C, and reactions were allowed to proceed until chlorine replacement had occurred, as indicated by ^{31}P NMR (24−48 h). The reaction mixtures were concentrated by rotary evaporation, and polymers **5**−**8** were purified by multiple precipitations into acidified water (pH ∼ 5) and methanol followed by drying on a vacuum line.

For **5:** tan, elastomeric polymer. Yield = 15.0 g (86%). ^{1}H NMR (d_8-THF): $\delta = 4.0$ (q, $J = 6.6$ Hz, 4H, OCH_2CH$_3$) 1.2 (t, $J = 6.8$ Hz, 6H, OCH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -7.8$ (s). Elemental analysis (calcd, found): N = (10.37, 9.98), P = (22.92, 22.88), C = (35.55, 35.47), H = (7.47, 7.37).

For **6:** white, elastomeric polymer. Yield = 17.0 g (81%). ^{1}H NMR (d_8-THF): $\delta = 3.9$ (q, $J = 6.4$ Hz, 4H, OCH_2CH$_2$CH$_3$), 1.6 (sx, $J = 7.1$ Hz, 4H, OCH$_2$CH_2CH$_3$), 0.9 (t, $J = 7.4$ Hz, 6H, OCH$_2$CH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -7.5$ (s). Elemental analysis (calcd, found): N = (8.59, 8.31), P = (18.98, 19.04), C = (44.16, 44.52), H = (8.66, 8.93).

For **7:** white, semicrystalline material. Yield = 16.1 g (77%). ^{1}H NMR (d_8-THF): $\delta = 4.7$ (2H, OCH(CH$_3$)$_2$), 1.3 (d, $J = 6.1$ Hz, 12H, OCH(CH_3)$_2$)). ^{13}C NMR (d_8-THF): $\delta = 22.2$ (4C, OCH(*C*H$_3$)$_2$), 66.9 (2C, O*C*H(CH$_3$)$_2$). ^{31}P NMR (d_8-THF): $\delta = -9.8$ (s). Elemental analysis (calcd, found): N = (8.59, 8.36), P = (18.98, 28.86), C = (44.16, 43.87), H = (8.66, 8.36).

For **8:** tan, elastomeric polymer. Yield = 26.9 g (85%). ^{1}H NMR (d_8-THF): $\delta = 4.0$ (t, $J = 6.2$ Hz, 4H, OCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.7 (mlt, $J = 7.1$ Hz, 4H, OCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.4 (mlt, 12H, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 0.9 (t, $J = 6.2$ Hz, 6H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -7.4$ (s). Elemental analysis (calcd, found): N = (5.66, 5.45), P = (12.52,12.02), C = (58.26, 57.00,), H = (10.62, 10.67).

Synthesis of Cosubstituted Polyphosphazenes (9−32). Sodium alkoxide solutions were prepared in distilled THF (75 mL) from ethanol, 1-propanol, 2-propanol, and 1-hexanol (16.9 mmol for reactions with **2**, 13.4 mmol for reactions with **3**, and 7.9 mmol for reactions with **4**) and sodium hydride (60%) (0.658 g, 16.5 mmol for reactions with **2**; 0.521 g, 13.0 mmol for reactions with **3**; and 0.315 g, 8.1 mmol for reactions with **4**). These solutions were added to solutions of **2**, **3**, and **4** (2.0 g, 8.2 mmol; 2.0 g, 6.5 mmol; and, 2.0 g, 3.94 mmol, respectively) in distilled THF (100 mL). Reactions were carried out at room temperature and at reflux in THF for each polymer/alkoxide reaction. The reaction mixtures were stirred for 48 h, concentrated by rotary evaporation, and purified by multiple precipitations into triply deionized water (pH ∼ 5),followed by multiple precipitations into hexanes. The cosubstituted polymers were then dried for 48 h in a vacuum oven at 55 °C to remove residual solvents. Typical yields ranged from 65 to 75% based on NMR calculation of side group ratios.

For **9:** white, elastomeric polymer. ^{1}H NMR (d_8-THF): $\delta =$ 4.5 (mlt, 4H, OCH_2CF$_3$), 4.0 (mlt, 4H, OCH_2CH$_3$) 1.2 (mlt, 6H, OCH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -7.3$, −5.8 (broad (br), overlapping (o)). ^{19}F NMR (d_8-THF): $\delta = -76.5$ (br, mlt). Elemental analysis (calcd, found): N = (7.05, 6.88), C = (24.17, 24.26), H = (3.28, 2.99), F = (33.83, 31.26).

For **10:** tan, elastomeric polymer. ^{1}H NMR (d_8-THF): $\delta =$ 4.5 (mlt, 4H, OCH_2CF$_3$), 4.0 (mlt, 4H, OCH_2CH$_3$) 1.2 (mlt, 6H, OCH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -7.2$, −7.0, −6.5 (br, o). ^{19}F NMR (d_8-THF): $\delta = -76.5$ (br, mlt). Elemental analysis (calcd, found): N = (7.81, 7.78), C = (26.78, 27.27), H = (4.25, 4.43), F = (26.05, 24.02).

For **11:** white gum. ^{1}H NMR (d_8-THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF$_3$), 3.9 (mlt, 4H, OCH_2CH$_2$CH$_3$), 1.6 (mlt, 4H, OCH$_2$CH_2CH$_3$), 0.9 (mlt, 6H, OCH$_2$CH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta =$ −8.0, −6.0 (br, o). ^{19}F NMR (d_8-THF): $\delta = -76.5$ (br, mlt). Elemental analysis (calcd, found): N = (6.38, 6.09), C = (24.94, 24.51), H = (3.16, 2.91), F = (37.39, 35.10).

For **12:** white, adhesive polymer. ^{1}H NMR (d_8-THF): $\delta =$ 4.5 (mlt, 4H, OCH_2CF$_3$), 3.9 (mlt, 4H, OCH_2CH$_2$CH$_3$), 1.6 (mlt, 4H, OCH$_2$CH_2CH$_3$), 0.9 (mlt, 6H, OCH$_2$CH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -8.0$, −6.0 (br, o). ^{19}F NMR (d_8-THF): $\delta = -76.2$ (br, mlt). Elemental analysis (calcd, found): N = (6.45, 6.55), C = (25.57, 25.18), H = (3.30, 3.18), F = (36.24, 31.76).

For **13:** white, semicrystalline material. ^{1}H NMR (d_8-THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF$_3$), 4.7 (s, br), 2H, OCH(CH$_3$)$_2$), 1.3 (mlt, 12H, OCH(CH_3)$_2$)). ^{31}P NMR (d_8-THF): $\delta = -7.7$, −7.1 (br, o). ^{19}F NMR (d_8-THF): $\delta = -76.2$ (br, mlt). Elemental analysis (calcd, found): N = (6.16, 6.19), C = (24.14, 23.97), H = (2.90, 2.60), F = (38.87,36.72).

For **14:** tan, semicrystalline material. ^{1}H NMR (d_8-THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF$_3$), 4.7 (s, br, 2H, OCH(CH$_3$)$_2$), 1.3 (d, 12H, OCH(CH_3)$_2$)). ^{31}P NMR (d_8-THF): $\delta = -7.7$, −7.1 (br, o). ^{19}F NMR (d_8-THF): $\delta = -76.2$ (br, mlt). Elemental analysis (calcd, found): N = (6.66, 6.33), C = (27.30, 27.22), H = (3.79, 3.92), F = (33.07, 30.22).

For **15:** off-white, elastomeric polymer. ^{1}H NMR (d_8-THF): $\delta = 4.5$ (mlt, 4H, OCH_2CF$_3$), 4.0 (mlt, 4H, OCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.7 (mlt, 4H, OCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.4 (mlt, 12H, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 0.9 (mlt, 6H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -8.0$, −6.1 (br, o). ^{19}F NMR (d_8-THF): $\delta = -76.1$ (br, mlt). Elemental analysis (calcd, found): N = (6.16, 5.59), C = (33.38, 32.62), H = (4.61, 4.65), F = (35.59, 30.66).

For **16:** tan, elastomeric polymer. ^{1}H NMR (d_8-THF): $\delta =$ 4.5 (mlt, 4H, OCH_2CF$_3$), 4.0 (mlt, 4H, OCH_2CH$_2$CH$_2$CH$_2$CH$_2$CH$_3$), 1.7 (mlt, 4H, OCH$_2$CH_2CH$_2$CH$_2$CH$_2$CH$_3$), 1.4 (mlt, 12H, OCH$_2$CH$_2$CH_2CH_2CH_2CH$_3$), 0.9 (mlt, 6H, OCH$_2$CH$_2$CH$_2$CH$_2$CH$_2$CH_3). ^{31}P NMR (d_8-THF): $\delta = -6.8$ (br, s). ^{19}F NMR (d_8-THF): $\delta = -76.1$ (br, mlt). Elemental analysis (calcd, found): N = (5.71, 5.44), C = (40.72, 41.07), H = (6.54, 6.63), F = (21.39, 19.84).

For **17:** white, semicrystalline material. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, OCH$_2$CF$_2$CF$_2$$H$), 4.4 (mlt, 4H, OC$H_2CF_2CF_2$H), 4.0 (mlt, 4H, OC$H_2CH_3$) 1.2 (mlt, 6H, OCH$_2CH_3$). ^{31}P NMR ($d_8$-THF): $\delta = -7.0$, −6.0 (br, o). ^{19}F NMR (d_8-THF): $\delta = -126.9$(s, br), −139.6 (s, br). Elemental analysis (calcd, found): N = (5.30,5.27), C = (25.01, 25.29), H = (2.68, 2.59), F = (43.16, 41.93).

For **18:** light brown, semicrystalline material. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 4.0 (mlt, 4H, $OC\mathit{H}_2CH_3$) 1.2 (mlt, 6H, $OCH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -7.0, -6.0$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -126.9$(s, br), -139.6 (s, br). Elemental analysis (calcd, found): N = (5.59, 5.52), C = (25.61, 26.35), H = (2.95, 2.89), F = (40.68, 38.22).

For **19:** white gum. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 3.9 (mlt, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.6 (mlt, 4H, $OCH_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -7.1, -5.9$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -128.3$ (s, br), -141.5 (s, br). Elemental analysis (calcd, found): N = (5.00, 4.88), *C* = (25.76, 24.82), H = (2.71, 2.49), F = (43.46, 40.71).

For **20:** tan, crystalline material. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 3.9 (mlt, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.6 (mlt, 4H, $OCH_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -7.1, -5.9$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -126.5$ (s, br), -139.6 (s, br). Elemental analysis (calcd, found): N = (5.11, 5.01), C = (26.29, 25.97), H = (2.89, 2.68), F = (42.71, 39.87).

For **21:** dark brown powder. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 4.7 (2H, $OC\mathit{H}(CH_3)_2$), 1.3 (mlt, 12H, $OCH(C\mathit{H}_3)_2$)). ^{31}P NMR (d_8-THF): $\delta = -7.0$ (br, s). ^{19}F NMR (d_8-THF): -126.9-(s, br), -139.6 (s, br). Elemental analysis (calcd, found): N = (4.88, 4.98), C = (25.11, 25.43), H = (2.51, 2.36), F = (45.55, 43.09).

For **22:** dark brown powder. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 4.7 (2H, $OC\mathit{H}(CH_3)_2$), 1.3 (mlt, 12H, $OCH(C\mathit{H}_3)_2$)). ^{31}P NMR (d_8-THF): $\delta = -7.0$ (br, s). ^{19}F NMR (d_8-THF): $\delta = -126.9$ (s, br), -139.6 (s, br). Elemental analysis (calcd, found): N = (5.00, 4.98), C = (25.76, 25.91), H = (2.71, 2.36), F = (43.46, 43.09).

For **23:** light brown gum. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 4.0 (t, 4H, $OC\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 1.7 (mlt, 4H, $OCH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 1.4 (mlt, 12H, $OCH_2CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$). ^{31}P NMR ($d_8$-THF): $\delta = -7.0, -6.2$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -128.1$ (s, br), -141.5 (s, br). Elemental analysis (calcd, found): N = (4.75, 4.72), C = (29.30, 28.96), H = (3.42, 3.17), F = (41.19, 37.90).

For **24**: dark brown gum. ^{1}H NMR (d_8-THF): $\delta = 6.1$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2\mathit{H}$), 4.4 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2H$), 4.0 (t, 4H, $OC\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 1.7 (mlt, 4H, $OCH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 1.4 (mlt, 12H, $OCH_2CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$). ^{31}P NMR ($d_8$-THF): $\delta = -7.0, -6.2$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -128.1$ (s, br), -141.5 (s, br). Elemental analysis (calcd, found): N = (4.84, 4.77), C = (32.39, 31.57), H = (4.19, 3.82), F = (36.79, 34.14).

For **25:** tan gum. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 4.0 (mlt, 4H, $OC\mathit{H}_2CH_3$) 1.2 (mlt, 6H, $OCH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -7.0, -6.0$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.20, 3.17), C = (24.37, 24.51), H = (1.56, 1.54), F = (56.42, 54.50).

For **26:** tan gum. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 4.0 (mlt, 4H, $OC\mathit{H}_2CH_3$) 1.2 (mlt, 6H, $OCH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -7.0, -6.0$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.32, 3.48), C = (24.55, 24.13), H = (1.78, 1.31), F = (55.52, 53.93).

For **27:** tan, adhesive polymer. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 3.9 (mlt, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.6 (mlt, 4H, $OCH_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -6.7, -5.9$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.22, 3.14), C = (25.32, 25.15), H = (1.78, 1.52), F = (55.22, 52.99).

For **28:** tan gum. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (mlt, $J = 52.5$, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 3.9 (mlt, 4H, $OC\mathit{H}_2CH_2CH_3$), 1.6 (mlt, 4H, $OCH_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2C\mathit{H}_3$). ^{31}P NMR (d_8-THF): $\delta = -6.7, -5.9$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.30, 3.39), C = (25.57, 25.37), H = (1.88, 1.61), F = (54.41, 53.97).

For **29:** light brown gum. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 4.7 (2H, $OC\mathit{H}(CH_3)_2$), 1.3 (mlt, 12H, $OCH(C\mathit{H}_3)_2$)). ^{31}P NMR (d_8-THF): $\delta = -7.0$ (br, s). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.12, 3.28), C = (24.95, 25.20), H = (1.66, 1.35), F = (56.24, 54.08).

For **30:** light brown gum. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 4.7 (2H, $OC\mathit{H}(CH_3)_2$), 1.3 (mlt, 12H, $OCH(C\mathit{H}_3)_2$)). ^{31}P NMR (d_8-THF): $\delta = -7.0$ (br, s). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.19, 3.28), C = (25.21, 24.61), H = (1.75, 1.70), F = (55.48, 53.27).

For **31:** tan gum. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t of t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$), 4.0 (mlt, 4H, $OC\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 1.7 (mlt, 4H, $OCH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 1.4 (mlt, 12H, $OCH_2CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$). ^{31}P NMR ($d_8$-THF): $\delta = -6.6, -5.8$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (2.99, 2.97), C = (26.42, 26.92), H = (1.94, 1.93), F = (55.19, 52.56).

For **32:** tan adhesive. ^{1}H NMR (d_8-THF): $\delta = 6.5$ (t of t, $J = 52.5$ Hz, 2H, $OCH_2CF_2CF_2CF_2CF_2\mathit{H}$), 4.3 (mlt, 4H, $OC\mathit{H}_2CF_2CF_2CF_2CF_2H$). 4.0 (mlt, 4H, $OC\mathit{H}_2CH_2CH_2CH_2CH_2CH_3$), 1.7 (mlt, 4H, $OCH_2C\mathit{H}_2CH_2CH_2CH_2CH_3$), 1.4 (mlt, 12H, $OCH_2CH_2C\mathit{H}_2C\mathit{H}_2C\mathit{H}_2CH_3$), 0.9 (mlt, 6H, $OCH_2CH_2CH_2CH_2CH_2C\mathit{H}_3$). ^{31}P NMR ($d_8$-THF): $\delta = -6.6, -5.8$ (br, o). ^{19}F NMR (d_8-THF): $\delta = -122.2$ (s, br), -126.3 (s, br), -131.1 (s, br), -139.5 (s, br). Elemental analysis (calcd, found): N = (3.03, 2.97), C = (26.82, 27.22), H = (2.05, 1.93), F = (54.49, 51.78).

Addition of 2,2,2-Trifluoroethoxide to Polymers 9, 10, 15, and 16. Sodium 2,2,2-trifluoroethoxide solutions in THF (75 mL) (2 equiv per repeat unit) were added to solutions of **9, 10, 15,** and **16** (1.0 g) in distilled THF (100 mL). The reaction mixtures were stirred for 48 h, concentrated by rotary evaporation, and purified by multiple precipitations into acidified water (pH ~ 5) and hexanes. The polymer composition remained the same as determined by ^{1}H NMR spectroscopy.

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References and Notes

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