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Polyphosphazenes with Adamantyl Side Groups

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ABSTRACT: Poly[bis(adamantylamino-*co*-trifluoroethoxy)phosphazene], poly[bis(adamantyloxy-*co*-trifluoroethoxy)phosphazene], and poly[bis(adamantylmethoxy-*co*-trifluoroethoxy)phosphazene] with different ratios of adamantyl to trifluoroethoxy groups were synthesized by macromolecular substitution. This work was preceded by model compound studies with cyclophosphazene trimers and tetramers. Polymers in which all the side groups were adamantyl units could not be prepared because of the steric restrictions imposed by the side groups. However, the mixed-substituent polymers with trifluoroethoxy cosubstituents were accessible by sequential substitutions on poly(dichlorophosphazene). These reactions were complicated by some displacement of adamantyl groups by the second nucleophile—sodium trifluoroethoxide. The molecular and materials properties of the mixed-substituent polymers are described.

Introduction

Adamantane (tricyclo[3.3.1.1^{3,7}]decane) is a highly symmetric, thermodynamically stable cage compound with the same framework structure as a diamond lattice. The unusual structure of adamantane imparts many useful chemical and physical properties, such as high thermal and oxidative stabilities, extreme lipophilicity, low surface energy, and high density.[1,2] Adamantane and its derivatives have found uses that range from lubricants[2,3] to pharmaceuticals.[4,5] Adamantyl groups have been incorporated into the main chain or side groups of polymers in an effort to take advantage of the special properties of the adamantane structure. Polymers that bear adamantyl moieties include polyacrylates,[6−8] polyamides,[9] thermoset resins,[10] and other materials.[11−15] These polymers generally possess improved thermal resistance and oxidative stability, raised melting point and glass transition temperatures, high dimensional stability, and improved solvent or hydrolysis stability. Our interest in adamantyl-containing polyphosphazenes was prompted by the possibility that they might show similar useful characteristics.

Polyphosphazenes are high-molecular-weight polymers which contain a backbone of alternating phosphorus and nitrogen atoms and with two organic, organometallic, or inorganic side groups linked to each skeletal phosphorus atom. Most polyphosphazenes are synthesized by macromolecular substitution reactions carried out on poly(dichlorophosphazene).[16,17] The macromolecular substitution method allows the introduction of a wide range of side groups and, hence, provides access to many different properties. For example, the incorporation of different side groups leads to the formation of low-temperature elastomers,[18−20] microcrystalline materials,[17] or brittle glasses. Several polyphosphazenes have shown useful membrane behavior, and in particular polymers with trifluoroethoxy side groups have a very high oxygen permeability.[21]

The incorporation of the bulky adamantyl moiety into the side-group structure of a polyphosphazene should hinder long-range molecular motion, raise the glass transition temperature, enhance the hydrophobicity, and perhaps exert a strong influence on the ability of the polymer to transmit gaseous molecules or organic liquids. In an earlier report, we described a series of small-molecule model compound experiments that indicated the feasibility of linking adamantyl groups to a phosphazene skeleton.[22] In the present study, we have extended these investigations at both the small-molecule and phosphazene high polymer levels and have attempted to answer the following questions: (1) What is the most practical method for the linkage of adamantyl side groups to a polyphosphazene? (2) What is the maximum "loading" of adamantyl groups possible both with and without spacer units between the adamantyl group and the polyphosphazene skeleton? (3) How high can the T_g of a polyphosphazene be raised by the utilization of adamantyl groups? (4) What is the influence of different spacer linkages to the adamantyl group on the glass transition temperature? The question of the influence of adamantyl groups on permselectivity will be addressed in a future publication.

Results and Discussion

Model Compound Studies. The macromolecular substitution reactions of halogenophosphazene high polymers are known to be sensitive to the steric bulk of the incoming nucleophile. For example, the replacement of the chlorine atoms in poly(dichlorophosphazene) by bulky aryloxy or arylamino groups often requires forcing experimental conditions and may in some circumstances lead to only incomplete halogen replacement.[23] Adamantyl groups are sufficiently bulky that questions existed about the feasibility of linkage of substantial numbers of these units to a polyphosphazene structure. For this reason, it was necessary to examine the ease of linkage of adamantyl groups to small-molecule cyclic trimeric and tetrameric phosphazenes in which the side-group−side-group steric restrictions would be minimized and a detailed characterization of the products would be possible.

The reactions were modeled using hexachlorocyclotriphosphazene, $(NPCl_2)_3$ (**1**), and octachlorocyclotetraphosphazene, $(NPCl_2)_4$ (**2**), as small-molecule analogues of poly(dichlorophosphazene), $(NPCl_2)_n$ (**3**). The nucleophiles employed are depicted as **4**−**6**. Thus, $(NPCl_2)_3$ and $(NPCl_2)_4$ were allowed to react in THF with a large excess (3 equiv per chlorine) of adamantanamine (**4**), with sodium adamantane oxide (**5**), or with sodium adamantane methoxide (**6**) to determine the most favorable reaction conditions and estimate the maximum loading of each side group. In the presence of triethylamine as a hydrogen chloride acceptor, **4** reacts readily

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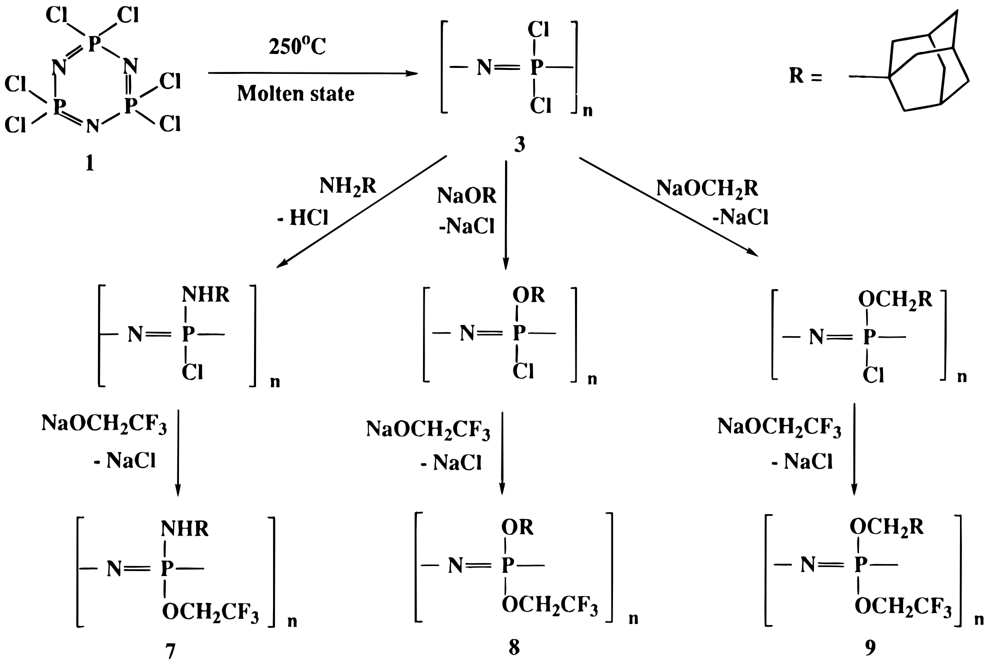
Scheme 1



Note that the disposition of the two types of side groups along the chains may be different from that shown.

with $(NPCl_2)_3$ to yield a mixture of tetra- and hexa-substituted products and with $(NPCl_2)_4$ to give the octa-substituted product.[24] Because reagent **5** is insoluble in THF and **6** has only a minimal solubility, tetra-*n*-butylammonium bromide was added to these reaction mixtures as a phase-transfer agent. The reaction of **5** with $(NPCl_2)_3$ and $(NPCl_2)_4$ yielded a mixture of only partially-substituted products. The interaction of **6** with $(NPCl_2)_3$ and $(NPCl_2)_4$ gave the fully substituted products in both cases.

The conclusions from the model compound work are that complete replacement of all the chlorine atoms in $(NPCl_2)_3$ and $(NPCl_2)_4$ is possible with the amino reagent **4** and with the alkoxide that bears the methylene spacer group (**6**) but that incomplete substitution occurs when the reagent is **5**. This incomplete replacement may be due to the proximity of the bulky unit to the reactive site of the nucleophile or to the low solubility of the reagent in the reaction medium.

Macromolecular Reactions. In contrast to the behavior of the small-molecule models, the reaction of high polymeric **3** with a large excess of **4** plus triethylamine or with **5** yielded polymers with a maximum of only 50% chlorine replacement, as estimated by ^{31}P NMR spectroscopy. The replacement of chlorine atoms by **6** was above 75% as estimated by ^{31}P NMR spectroscopy. This higher reactivity is probably due to the lower steric hindrance and higher flexibility of the adamanylmethoxy group compared to the adamantylamino and adamantyloxy groups, as well as to the slight increase in solubility of **6** compared to **5**.

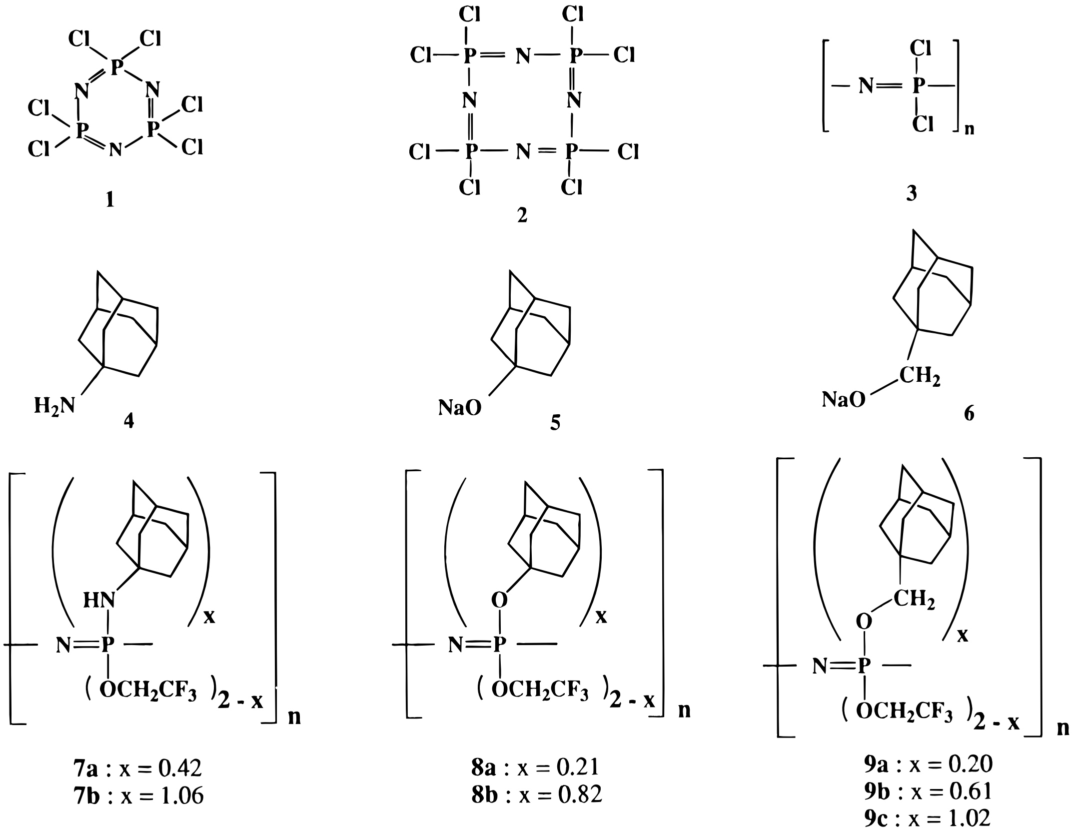
The conclusions from this phase of the work were that complete replacement of all the chlorine atoms in poly(dichlorophosphazene) by adamantyl groups is not possible under the reaction conditions employed. The presence of unreacted phosphorus–chlorine units is likely to lead to long-term hydrolytic instability. Thus, it was necessary to replace the residual chlorine atoms with the use of a less hindered and more reactive reagent. The nucleophile chosen was sodium trifluoroethoxide.

The protocol followed in this phase of the work was to first synthesize a series of polymers with different ratios of the adamantyl side group to unreacted chlorine, as shown in Scheme 1. Specifically, the preparation of two polymers was attempted with the adamantylamino unit constituting 20% and 50% respectively of the total side groups present, two polymers with adamantyloxy groups also present as 20% and 50% of the total side units, and three polymers with 20%, 50%, and 70% adamantylmethoxy side groups. These were characterized by ^{31}P NMR spectroscopy to determine the side-group ratios, and the polymers were then treated with an excess of sodium trifluoroethoxide. Purification of the polymers was followed by examination of them by elemental microanalysis, NMR spectroscopy, gel permeation chromatography, and thermal analysis.

The theoretical ratios of adamantyl units to trifluoroethoxy side groups are 1:4 (**7a**, **8a**, **9a**; $x = 0.4$, 20% substitution by the adamantyl group), 1:1 (**7b**, **8b**, **9b**; $x = 1.0$, 50% substitution), and 1:0.43 (**9c**; $x = 1.4$, 70% substitution), where x is the fraction of mole ratio of adamantyl groups per monomeric unit (see Chart 1). Experimental values for the side-group ratios were determined by integration of the ^1H NMR spectra and from the elemental analyses of the polymers and are listed in Table 1. The values determined by the two methods agreed within 5% ($x \pm 0.1$). For polymers **7a** and **7b**, the expected and found percent substitutions by adamantanamine on **3** are in close agreement.

However, for polymers **8a**, **8b**, **9a**, **9b**, and **9c**, the final level of adamantyl substitution was found to be significantly lower than expected (see Table 1). For these systems, it appears that the sodium trifluoroethoxide reagent displaced some of the adamantyloxy or adamantylmethoxy groups from phosphorus. It has been shown previously that sodium trifluoroethoxide can replace phenoxy or methoxyethoxyethoxy side groups

Chart 1



1

2

3

4

5

6

7a : x = 0.42
7b : x = 1.06

8a : x = 0.21
8b : x = 0.82

9a : x = 0.20
9b : x = 0.61
9c : x = 1.02

Table 1. Polymer Characterization Data

	x	% adamantyl[a]	% Cl	M_{GPC}	PDI
7a	0.42	21 (20)	1.22	130 000	1.4
7b	1.06	53 (50)	1.72	290 000	2.2
8a	0.21	10 (20)	0.43	140 000	1.7
8b	0.82	41 (50)	1.51	400 000	3.5
9a	0.20	10 (20)	0.21	860 000	2.1
9b	0.61	30 (50)	0.29	530 000	1.8
9c	1.02	51 (70)	0.26	560 000	2.0

[a] The values in parentheses are the target levels of substitution.

from polyphosphazenes.[25] When fewer equivalents of $NaOCH_2CF_3$ per remaining chlorine were used in the cosubstitution, the ratio of the adamantyl groups to trifluoroethoxy units was closer to the intended value. For example, in the synthesis of **8b**, 1.5 equiv of $NaOCH_2CF_3$ per remaining chlorine atom was used, while for the other polymers (**8a**, **9a**, **9b**, and **9c)** 3 equiv per remaining chlorine were employed. The adamantyloxy side group was incorporated into **8b** at a level of 41% (instead of 50% as initially expected), while for **9b** the incorporation was only 30% instead of 50%, and for **8a** only 10% instead of 20%. However, the use of a smaller excess of sodium trifluoroethoxide to retain more of the adamantyl units involves a significant trade-off because the final amount of unreacted chlorine was much higher in **8b** than in the other polymers that contained adamantyloxy and adamantylmethoxy units. Clearly, the final outcome from these reactions depends on a balance between removal of all the chlorine atoms and avoidance of displacement of the adamantyl groups already present. This is an important consideration because residual P−Cl units can give rise to hydrolytic instability, which eventually leads to chain cleavage. This may be the reason for the high polydispersity index found for **8b** (Table 1).

Polymers **7a** and **7b** also had a high percentage of chlorine based on elemental analysis. We believe that most of this chlorine content reflects the presence of hydrogen chloride coordinated to the backbone or side-group nitrogen atoms of the polymer. Polymer **7b** showed no sign of hydrolytic degradation during a period of 1 year, and this suggests that few if any residual P−Cl units are present.

The overall conclusions from the synthesis of the mixed-substituent polymers are as follows: (1) Forcing reaction conditions (refluxing solvents, large excess of the second nucleophile, and long reaction times) are needed to yield polymers with minimal amounts of residual chlorine (less that 0.5% in most cases). (2) THF is the preferred solvent for these reactions, since other higher boiling solvents, such as dioxane or toluene, bring about precipitation of the chlorophosphazene polymer and a termination of further substitution when less than 10% of the chlorine has been replaced by adamantyl units. (3) It seems clear that the use of adamantylamine as a reagent offers the most controllable way to introduce adamantyl side groups into a polyphosphazene.

Characterization and Materials Properties. Tables 1 and 2 summarize the GPC molecular weights and molecular weight distributions of the mixed-substituent polymers and the thermal transitions detected mainly by thermomechanical analysis. Classical differential scanning calorimetry experiments were relatively insensitive to the presence of transitions in these polymers. As shown in Table 1, the polymer molecular weights ranged from 130 000 to 860 000, which corresponds approximately to from 500 to 3000 repeating units per chain. The polydispersity indices are quite broad (1.4−3.5), which is a common feature of polyphosphazenes synthesized by these techniques. As shown in Table 2, the introduction of adamantyl side groups brings about a dramatic increase in the glass transition

Table 2. TMA Data and Film Characteristics

	thermal trans., °C	film thickness, mm	film characteristics
7a (21%)[a]	$T_g = 40$ $T_1 = 82$	0.29	transparent, rigid
7b (53%)[a]	$T_g = 180$ $T_1 = 200$	0.22	opaque, rigid
8a (10%)[a]	$T_x = 44$[b]	0.32	transparent, flexible
8b (41%)[a]	$T_g = 46$ $T_1 = 75$	0.43	opalescent, rigid
9a (10%)[a]	$T_g = -44$ $T_1 = 52$	0.32	opalescent, flexible
9b (30%)[a]	$T_g = 25$ $T_1 = 59$	0.41	opalescent, leathery
9c (51%)[a]	$T_g = 61$ $T_1 = 91$	0.68	opaque, rigid
$[NP(OCH_2CF_3)_2]_n$[c] (0%)[a]	$T_g = -66$ $T_1 = 40$ $T_m = 210$	0.40	opalescent, flexible

[a] Percent adamantyl content (molar). [b] This transition was detected by TMA only, and it was not possible to identify it as a T_g or T_1. [c] Used as a control: values given are from TMA data.

temperature, compared to the value of −66 °C for the control polymer, $[NP(OCH_2CF_3)_2]_n$, with values that range from −44 to +180 °C depending on the loading and type of adamantyl unit. No T_g was detected for **8a**, even though this sample was run several different times under different conditions. The highest glass transition (+180 °C) was found for polymer **7b** which had a 53% loading of the adamantanamino unit. This appears to be the highest T_g reported yet for a polyphosphazene. Various T_1 transitions were also detected as listed in Table 2.

Explanation of Materials Properties. The phosphorus−nitrogen backbone is highly flexible, and in the absence of other factors, polyphosphazenes show very low glass transition temperatures. Thus, polymers that bear small or highly flexible side groups can have T_g values in the region of −100 °C. For example, $[NP(OCH_2CH_2CH_2CH_3)_2]_n$ has a T_g of −105 °C. However, polar, coordinative, or bulky side groups raise the T_g by restricting the torsional motions of the chain through intramolecular dipolar, hydrogen bonding, or steric interactions. As mentioned above, when the butoxy groups are replaced by OCH_2CF_3 groups, the T_g rises to −66 °C. Two phenoxy groups per phosphorus increase the T_g to −8 °C. Two phenylamino groups per phosphorus raise the value to +91 °C. One of the highest T_g's recorded earlier for a polyphosphazene was the value of 111 °C for a polymer with para-substituted biphenylenemethoxy side groups.[26] The T_g value of +180 °C for **7b** almost certainly reflects the ability of the adamantylamino side groups to restrict polymer chain motions by both steric interference and hydrogen bonding, even when nearly half of the side groups present are trifluoroethoxy units.

Experimental Section

Materials. Hexachlorocyclotriphosphazene (**1**) was obtained from Ethyl Corp. and was purified by recrystallization from hexane, followed by sublimation at 40 °C (0.05 Torr). Poly(dichlorophosphazene) (**3**) was prepared by the ring-opening polymerization of **1** at 250 °C.[16] The residual cyclic phosphazenes were removed from **3** by sublimation at 60 °C (0.05 Torr), and the purity of the polymer was verified by ^{31}P NMR spectroscopy. Tetrahydrofuran (THF) was dried by distillation from sodium benzophenone ketyl, triethylamine was distilled from sodium, and trifluoroethanol was distilled from calcium hydride, all under argon. Adamantanamine, adamantanol, and adamantanemethanol (Aldrich or Acros) were purified by sublimation. All other reagents (Aldrich or Fluka) were used as received.

Instrumentation and Methods. All reactions were carried out with the use of conventional inert-atmosphere techniques. High-field ^{31}P (146-MHz), ^{13}C (90-MHz), and ^{1}H (360 MHz) NMR spectra were obtained by use of a Brucker WM360 spectrometer. Both ^{31}P and ^{13}C spectra were proton decoupled. ^{31}P NMR spectra were referenced to external 85% H_3PO_4 with positive shifts recorded downfield of the reference. ^{13}C and ^{1}H NMR spectra were referenced to external tetramethylsilane. Elemental analyses were obtained by Quantitative Technologies, Inc., Whitehouse, NJ. Molecular weights were estimated by use of a Hewlett-Packard HP1090 gel-permeation chromatograph equipped with an HP-1047A refractive index detector and Polymer Laboratories PL gel 10-mm columns. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium nitrate in THF. The GPC columns were calibrated with polystyrene standards (Waters). Glass transition temperatures were determined by differential scanning calorimetry (DSC) and thermal mechanical analysis (TMA) using a Perkin-Elmer 7 thermal analysis system equipped with a Perkin-Elmer 7500 computer. The polymers were purified by multiple precipitations, and the final yields were in the range of 10−30% depending on the efficiency of the precipitation processes.

Synthesis of Poly[bis(adamantylamino-*co*-trifluoroethoxy)phosphazenes] (7a and 7b). The synthesis of **7b** is given as an example. A solution of adamantanamine (5.22 g, 0.034 mol) and triethylamine (7.5 mL, 0.053 mol) as a hydrogen chloride acceptor in 180 mL of THF was added dropwise to **3** (4.0 g, 0.034 mol per $NPCl_2$) dissolved in 400 mL of THF. The reaction mixture was stirred for 48 h in refluxing THF. Sodium trifluoroethoxide ($NaOCH_2CF_3$) was prepared by adding dropwise trifluoroethanol (7.5 mL, 0.103 mol) to sodium metal (2.38 g, 0.103 mol) in 200 mL of THF. The sodium trifluoroethoxide solution was added dropwise to the polymer solution, and the reaction mixture was stirred and heated at reflux for 48−72 h. The reaction mixture was filtered and concentrated on a rotary evaporator. The concentrated solution was precipitated into 2 L of distilled water to yield a white material. The polymer was then purified by repeated precipitations from THF into water and methanol. **7b**: ^{31}P NMR (d_1-$CDCl_3$), δ (ppm) −4.4 (very br, 0 to −15). ^{1}H NMR (d_1-$CDCl_3$), δ (ppm) 4.35 (1.3 H), 3.57 (0.6 H), 2.3−1.5 (15 H). ^{13}C NMR (d_1-$CDCl_3$), δ (ppm) 125, 77.2, 63.0, 44.6, 36.3, 29.8. Elemental Anal. Calcd: C, 50.41; H, 6.34; N, 9.71. Found: C, 50.54; H, 6.21; N, 9.50; Cl, 1.72. Polymer **7a** was synthesized in an analogous manner and was purified by repeated precipitations from THF into water and hexane. Polymer **7a** is soluble in methanol. **7a**: ^{31}P NMR (d_1-$CDCl_3$), δ (ppm) −3.4 (smaller), −7.1 (sh), −8.5. ^{1}H NMR (d_1-$CDCl_3$), δ (ppm) 4.26 (6.4 H), 3.55 (0.6 H), 2.1−1.5 (15 H). ^{13}C NMR (d_1-$CDCl_3$), δ (ppm) 124, 77.2, 63.2, 44.1, 35.9, 29.7. Elemental Anal. Calcd: C, 33.11; H, 3.74; N, 7.52. Found: C, 33.21; H, 3.89; N, 7.79; Cl, 1.22.

Synthesis of Poly[bis(adamantyloxy-*co*-trifluoroethoxy)phosphazenes] (8a and 8b). Polymer **8a** was synthesized as follows: Adamantanol (2.10 g, 0.013 mol) was added under positive argon pressure to a slurry of NaH dispersion (60% by weight, 0.52 g, 0.013 mol of NaH) and *n*-Bu_4NBr (0.44 g, 0.0013 mol) in 160 mL of THF. The mixture was refluxed overnight to form the sodium salt. The salt solution was added dropwise to a solution of **3** (4.0 g, 0.034 mol of $NPCl_2$) in 400 mL of THF. The reaction mixture was stirred and heated at reflux for 48 h. A solution of sodium trifluoroethoxide in THF was added dropwise. The sodium trifluoroethoxide was prepared as described for **7b** from trifluoroethanol (12 mL, 0.16 mol) and sodium (3.81 g, 0.16 mol). The reaction mixture was stirred for 72 h. The mixture was then filtered and concentrated on a rotary evaporator. The concentrated polymer solution was precipitated into 2 L of water to give a yellowish material. The polymer was purified by repeated precipitations from THF into water and hexane. Polymer **8a** is soluble in methanol. **8a**: ^{31}P NMR (d_4-MeOH), δ (ppm) −8.0, −11.6 (small). ^{1}H NMR (d_4-MeOH), δ (ppm) 4.38 (13.8 H), 2.11 (7.8 H), 1.66 (6 H). ^{13}C NMR (d_4-MeOH), δ (ppm) 124, 77.2, 64.5, 44.4, 36.7, 32.6. Elemental Anal. Calcd: C, 26.84; H, 2.65; N, 5.52. Found: C, 26.86; H, 2.77; N, 5.69; Cl, 0.43.

Polymer **8b** was synthesized as follows: Adamantanol (3.17 g, 0.021 mol) was added under positive argon pressure to a slurry of NaH dispersion 60% by weight (0.69 g, 0.017 mol of NaH) and *n*-Bu$_4$NBr (0.59 g, 0.0018 mol) in 175 mL of THF. The mixture was heated at reflux overnight to form the sodium salt. The salt solution was then added dropwise to a solution of **3** (2.0 g, 0.017 mol of NPCl$_2$) in 250 mL of THF. The reaction mixture was stirred and heated at reflux for 48 h. A solution of sodium trifluoroethoxide in THF was added dropwise. The sodium trifluoroethoxide was prepared as for **7b** from trifluoroethanol (2.2 mL, 0.030 mol) and sodium (0.60 g, 0.026 mol). The mixture was then stirred for 96 h. The reaction mixture was filtered and concentrated on a rotary evaporator. The concentrated polymer solution was precipitated into 2 L of methanol to give an off-white material. The polymer was purified by repeated precipitations from THF into methanol and water. **8b**: ^{31}P NMR (d_1-CDCl$_3$), δ (ppm) −10.4, −12.1, −14.1 (t), −20.7 (very small). ^{1}H NMR (d_1-CDCl$_3$), δ (ppm) 4.26 (2.0 H), 2.14 (9.6 H), 1.61 (6 H). ^{13}C NMR (d_1-CDCl$_3$), δ (ppm) 124, 78.2, 62.8, 43.3, 35.9, 31.2. Elemental Anal. Calcd: C, 44.36; H, 5.13; N, 4.90. Found: C, 44.28; H, 5.37; N, 4.92; Cl, 1.51.

Poly[bis(adamantylmethoxy-*co*-trifluoroethoxy)phosphazenes] (9a, 9b, and 9c). The synthesis of **9b** was typical. Adamantanemethanol (5.74 g, 0.034 mol) was added under positive argon pressure to a slurry of NaH dispersion 60% by weight (1.38 g, 0.034 mol of NaH) and *n*-Bu$_4$NBr (1.11 g, 0.0034 mol) in 200 mL of THF. The mixture was refluxed overnight to form the sodium salt. The salt solution then was added dropwise to a solution of **3** (4.0 g, 0.034 mol of NPCl$_2$) in 500 mL of THF. The reaction mixture was stirred and heated at reflux for 48 h. A solution of sodium trifluoroethoxide in THF was then added dropwise. The sodium trifluoroethoxide was prepared as for **7b** from trifluoroethanol (7.5 mL, 0.102 mol) and sodium (2.38 g, 0.103 mol). The reaction mixture was stirred for 48−72 h before being filtered and concentrated on a rotary evaporator. The concentrated polymer solution was precipitated into 2 L of water. The polymer was then purified by repeated precipitations from THF into methanol and water. **9b**: ^{31}P NMR (d_1-CDCl$_3$), δ (ppm) −6.4, −8.2. ^{1}H NMR (d_1-CDCl$_3$), δ (ppm) 4.22 (4.5 H), 3.46 (2 H), 1.94 (2.7 H), 1.64 (q, 8.2 H), 1.46 (7.4 H). ^{13}C NMR (d_1-CDCl$_3$), δ (ppm) 123, 77.5, 63.0, 38.7, 36.8, 33.5, 27.9. Elemental Anal. Calcd: C, 40.20; H, 4.64; N, 4.94. Found: C, 40.27; H, 4.88; N, 5.06; Cl, 0.29. Polymer **9a** was synthesized in an analogous manner and purified by repeated precipitations from THF into water and hexane. Polymer **9a** is soluble in methanol. **9a**: ^{31}P NMR (d_8-THF), δ (ppm) −6.1 (small), −7.3. ^{1}H NMR (d_8-THF), δ (ppm) 4.42 (11.6 H), 2.72 (2 H), 1.97 (2.7 H), 1.70 (q), 1.58. ^{13}C NMR (d_8-THF), δ (ppm) 124, 76.0, 63.9, 39.6, 37.7, 35.4, 29.1. Elemental Anal. Calcd: C, 27.17; H, 2.73; N, 5.47. Found: C, 27.28; H, 2.85; N, 5.69; Cl, 0.21. Polymer **9c** was also synthesized in an analogous manner to **9b** and was purified by repeated precipitations from THF into water and methanol. **9c**: ^{31}P NMR (d_1-CDCl$_3$), δ (ppm) −6.9, −8.9 (small). ^{1}H NMR (d_1-CDCl$_3$), δ (ppm) 4.26 (1.8 H), 3.50 (2 H), 1.96, 1.68 (q), 1.52. ^{13}C NMR (d_1-CDCl$_3$), δ (ppm) 123, 77.5, 62.5, 38.9, 36.9, 33.5, 28.0. Elemental Anal. Calcd: C, 50.97; H, 6.22; N, 4.51. Found: C, 51.21; H, 6.18; N, 4.59; Cl, 0.26.

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