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Poly(thiophosphazenes): New Inorganic Backbone Polymers

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ABSTRACT: The cyclic thiophosphazene $N_3P_2SCl_5$ undergoes thermal ring-opening polymerization when heated at 90 °C. The resultant polymer, $[N_3P_2SCl_5]_n$, is a hydrolytically sensitive, yellow, elastomeric material. This polymer reacts with aryloxide nucleophiles to give poly[(aryloxy)thiophosphazenes] of general structure $[N_3P_2S(OAr)_xCl_y]$ $(x > y)$. The structures of these polymers were examined with the use of ^{1}H and ^{31}P NMR spectroscopy, elemental microanalysis and gel permeation chromatography. The glass transition temperatures of the polymers were measured by means of differential scanning calorimetry and were found to be in a range from −40 to +79 °C. These T_g values are compared to those of poly(carbophosphazene) and classical phosphazene analogues. Reactions of $N_3P_2SCl_5$ with $NaOCH_2CF_3$ and NaOPh–Ph-*o* are also described.

Introduction

Ring-opening and condensation polymerization provide the main synthetic routes to inorganic polymers.[1] Several new polycondensation syntheses to inorganic macromolecules have been discovered in recent years,[2] but relatively few inorganic ring systems are known that will undergo ring-opening polymerization. The main impetus for research in these areas is the development of new polymeric materials that possess new combinations of properties not found in conventional organic polymers.

Polyphosphazenes form a broad class of inorganic macromolecules with backbones composed of alternating phosphorus and nitrogen atoms.[3] The most widely used synthetic route to these materials is through the thermal ring-opening polymerization of hexachlorocyclotriphosphazene (**1**) to give poly(dichlorophosphazene) (**2**) which serves as a synthetic intermediate for the preparation of derivatives of general structure **3** (Scheme I).

The ring-opening polymerization of cycloheterophosphazenes is a new area of research that provides access to hitherto unknown types of inorganic polymers.[4] These new polymers contain backbone heteroatoms in addition to phosphorus and nitrogen. The resultant polymers are structurally similar to the classical polyphosphazenes, but they have different physical properties due to the different backbone structures.

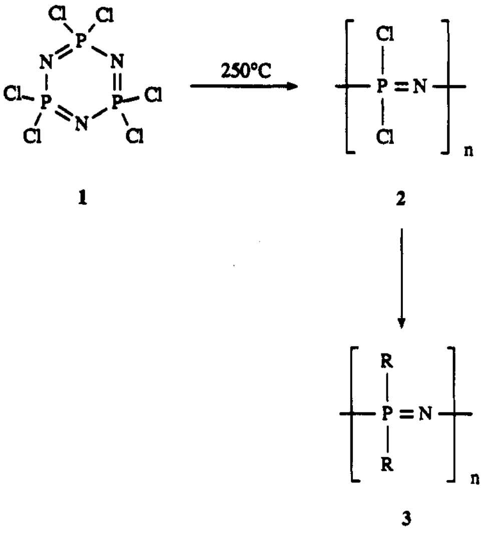
We describe here the results of our work on the synthesis and characterization of poly(thiophosphazenes), a new class of inorganic polymers.[4b] These macromolecules are obtained through the thermal ring-opening polymerization of cyclothiophosphazene **4** to give polymer **5** (Scheme II). Both **4** and **5** react with organic nucleophiles to give organothiophosphazene derivatives.

In the following discussion, the synthesis and characterization of **4** and **5** are described first. This is followed by a description of the preparation of poly[(aryloxy)thiophosphazene] and cyclothiophosphazene derivatives. Finally, the glass transition temperatures of the poly(thiophosphazenes) are compared with those of classical phosphazenes and carbophosphazene analogues.

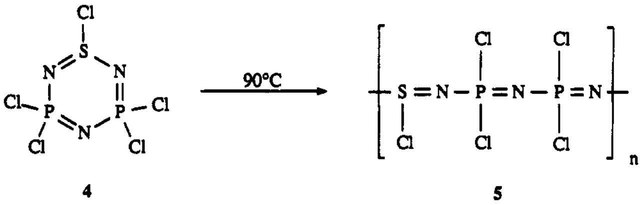
Results and Discussion

Synthesis and Ring-Opening Polymerization of 4. A previously reported synthetic route to **4**[5] was utilized during our initial experiments. However, it became clear that a higher yield synthesis of **4** was needed. It was found that cationic short-chain species **6** reacts in solution with bis[(trimethylsilyl)imido]sulfur (**7**) to give **4** in nearly quantitative yield (Scheme III). The product was isolated as a very pale green oil following vacuum distillation. The ^{31}P NMR spectrum of **4** consists of a singlet resonance at

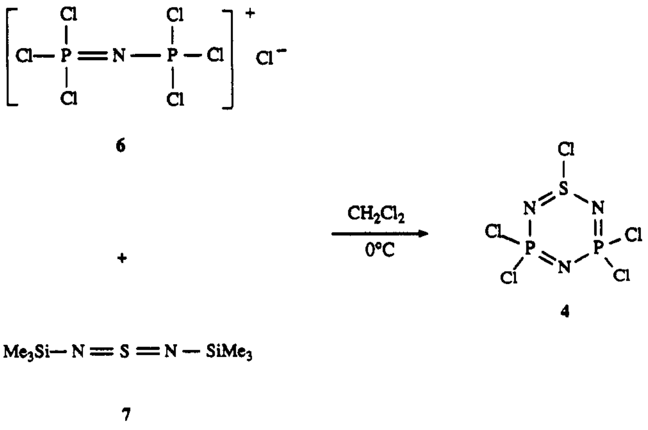
Scheme I



Scheme II



Scheme III



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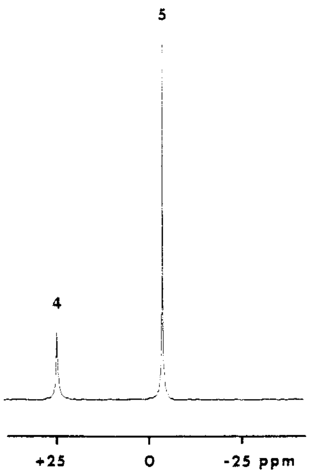
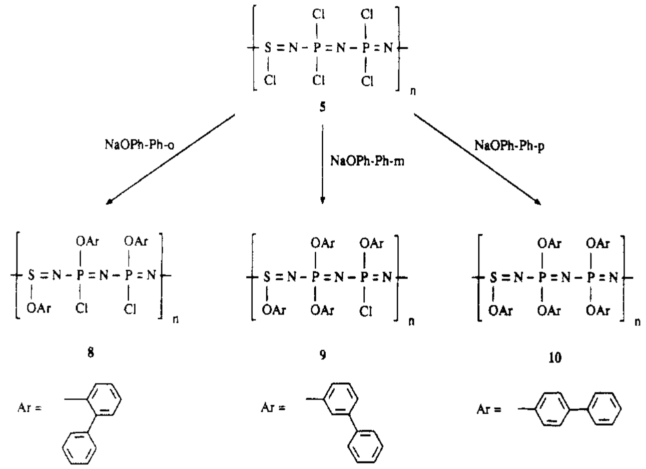


Figure 1. ^{31}P NMR spectrum after heating 4 at 90 °C for 5 h.

Scheme IV



24.5 ppm.[5] The electron-impact mass spectrum of the product contained an intense peak at m/e 278 $(M - Cl)^+$ with the appropriate isotope pattern for four chlorine atoms.

When heated under vacuum in a thick-walled Pyrex tube at 90 °C, samples of 4 turned amber in color and became highly viscous. After 4–5 h this temperature, the viscosity of the product had increased to the point that the material was nearly immobile.[6] Analysis of the products at this stage using ^{31}P NMR spectroscopy showed the presence of unreacted 4 and a new singlet resonance at −4.4 ppm (Figure 1). The product (5) was isolated by multiple reprecipitations from dioxane into n-heptane. Following drying under vacuum, polymer 5 was obtained as a hydrolytically sensitive, yellow, elastomeric material.

Structural characterization of 5 was accomplished by ^{31}P NMR analysis and elemental microanalysis. Due to its hydrolytic sensitivity, analysis by using gel permeation chromatography (GPC) was not attempted. The ^{31}P NMR spectrum of 5 consisted of a sharp singlet resonance at −4.4 ppm. A similar upfield shift of the ^{31}P NMR resonance occurs in the formation of 2 (−18.4 ppm) from 1 (19.9 ppm). The presence of a singlet resonance for 5 suggests that the polymer has a head-to-tail microstructure, since a head-to-head arrangement should give a more complex ^{31}P NMR spectrum.

The glass transition temperature (T_g) of 5 was measured by differential scanning calorimetry (DSC) and was found to be −40 °C. This value is higher than that for 2 (−63 °C)[3] and suggests that the torsional flexibility of the thiophosphazene backbone is lower than that of the classical phosphazene backbone (see below).

Synthesis of Poly[(aryloxy)thiophosphazenes] 8–12. As with poly(dichlorophosphazene) (2), polymer 5 can serve as a synthetic intermediate to organic derivatives. Initial substitution reactions were carried out using THF as solvent. However, it was found that compounds 4 and 5 initiated the ring-opening polymerization of THF, and poly(tetramethylene oxide)[7] could be isolated as a white polymeric material. Presumably, this is a consequence of the heterolytic cleavage of sulfur–chlorine bonds in these compounds. The resultant cationic species probably initiates the polymerization of THF. Therefore, all subsequent reactions of 4 and 5 were conducted using dioxane because this solvent resists ring-opening polymerization.

Aryloxide nucleophiles were used to prepare stable derivatives of 5 (Scheme IV).[8] The reaction of 5 with excess o-phenylphenoxide gave a partially substituted species represented as compound 8. Reprecipitations from dioxane into water and into hexanes, followed by drying under vacuum, gave 8 as an off-white, brittle, film-forming material. The ^{31}P NMR spectrum of 8 contained broad resonances at −12.3 and −16.9 ppm of approximately equal intensity. The latter peak was assigned to phosphorus atoms that bear either two chlorine atoms or one chlorine atom and one aryloxy group. The resonance at −12.3 ppm corresponds to $P(OAr)_2$ units. Thus, the schematic representation of 8 is oversimplified because both $P(Cl)_2$ and $P(OAr)_2$ groups are also present.

Elemental microanalysis was used to determine the level of aryloxy substitution in 8. The elemental ratios indicated that approximately 65% of the chlorine atoms in 5 had been replaced by aryloxy groups. In spite of the presence of unreacted P–Cl bonds, polymer 8 was sufficiently unreactive to withstand the aqueous isolation conditions. Similar results were obtained with the classical polyphosphazene analogue of 8, $[NP(OPh\text{–}Ph\text{-}o)_{1.52}Cl_{0.48}]_n$.[9] In both cases, the unreacted P–Cl bonds appear to be shielded from hydrolytic attack by the bulky aryloxy side groups.

Further structural confirmation for 8 was obtained by using ^{1}H NMR and GPC analyses. The weight average molecular weight (M_w) was estimated to be 3.1×10^5 and the number average molecular weight (M_n) was 1.0×10^5. Analysis of the material using DSC indicated a T_g of 79 °C.

Polymer 5 reacts with excess m-phenylphenoxide to give derivative 9 (Scheme IV). Following the isolation procedure as described for 8, polymer 9 was obtained as a brittle solid. However, unlike 8, the ^{31}P NMR spectrum of 9 showed a single broad resonance at −12.1 ppm. The broadness of the peak suggested that complete chlorine atom replacement had not occurred, but the presence of a single resonance was consistent with a much higher level of aryloxy substitution than for 8. This was confirmed by elemental microanalysis which indicated that only 12% of the chlorine atoms in 5 had not been replaced. This corresponds to a molecular formula of $[N_3P_2S(OPh\text{–}Ph\text{-}m)_{4.4}Cl_{0.6}]_n$. Further structural characterization was achieved by using ^{1}H NMR and GPC analyses. The T_g of the material was found to be 32 °C.

The reaction of 5 with sodium p-phenylphenoxide gave the polymer represented by structure 10 (Scheme IV). This product did not withstand the isolation conditions outlined above for 8 and 9, and a nonaqueous isolation procedure was therefore devised (see Experimental Section). In this way, polymer 10 could be isolated as a white material. Attempts to isolate polymers 8 and 9 by using a similar nonaqueous method did not improve on the results described above.

The molecular structure of **10** was confirmed using ^1H and ^{31}P NMR analysis, elemental microanalysis, and GPC. In this case, the ^{31}P NMR spectrum consisted of a single, relatively sharp resonance at -11.0 ppm. This suggests a higher degree of aryloxy substitution than for **9**. The results of elemental microanalysis confirmed this and suggested that only 6% of the chlorine atoms remained. Thus, the molecular formula is $[N_3P_2S(OPh\text{-}Ph\text{-}p)_{4.7}Cl_{0.3}]_n$. DSC analysis was used to determine the T_g of the material, which was found to be 69 °C.

Efforts to increase the loading of organic side groups in **8**–**10** by warming the reaction mixtures, using a larger excess of nucleophile, or by extended reaction times, invariably resulted in skeletal cleavage, as indicated by ^{31}P NMR and/or GPC analysis. Each synthesis of **8**–**10** was repeated at least once under the conditions described in the Experimental Section. The data listed represent the results obtained for the best materials.

During the course of this work, ^{31}P NMR analysis revealed that the S–Cl bond in compounds **4** and **5** is much more reactive toward nucleophilic substitution than the P–Cl bonds. Exclusive substitution at sulfur can be achieved under carefully controlled reaction conditions. The following cosubstituent polymer was prepared by utilizing this reactivity difference.

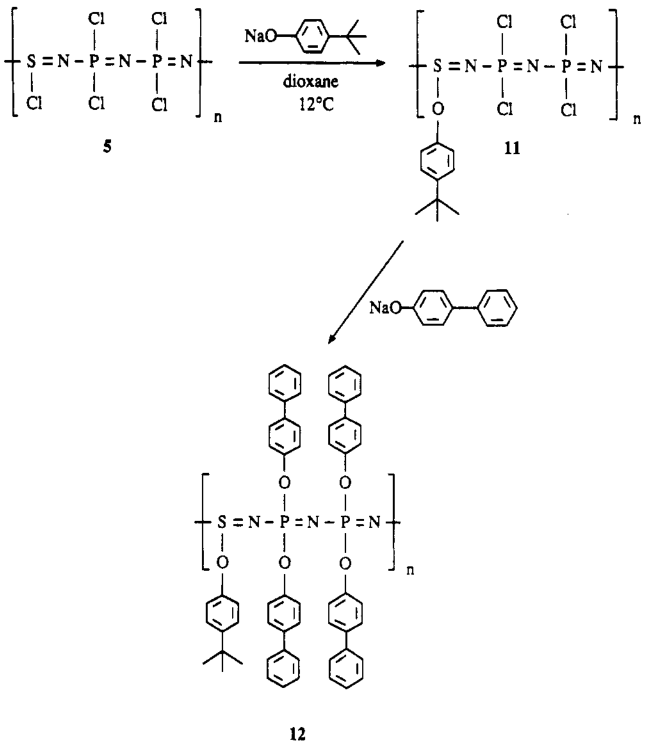
A solution of sodium *p-tert*-butylphenoxide (1 equiv) was slowly added to a dioxane solution of **5** at 12 °C. Analysis of the reaction mixture using ^{31}P NMR spectroscopy showed the disappearance of the resonance of **5** and the formation of a single new resonance at -7.3 ppm. This resonance shift falls between that of **5** and those of polymers **8**–**10** and probably corresponds to compound **11** (Scheme V). Excess NaOPh–Ph-*p* was then added. After the reaction mixture had been stirred at room temperature for 3 days, product **12** was isolated in a manner similar to that described for **10**. The ^{31}P NMR spectrum of **12** consists of a sharp singlet resonance at -11.2 ppm. Further structural characterization was obtained by using ^1H NMR and GPC analyses. Elemental microanalysis was used to determine the loading of aryloxy groups. The elemental ratios indicated that the molecular structure was $[N_3P_2S(OPh\text{-}Ph\text{-}p)_{3.6}Cl_{0.4}(OPh\text{-}{}^tBu\text{-}p)_{1.0}]_n$.

Room-Temperature Polymerization of 4. Certain samples of **4** that had been stored at room temperature in Pyrex vessels became yellow and highly viscous. After several weeks, these samples often developed an elastomeric character but were insoluble in dioxane, presumably due to cross-linking. In a controlled experiment, constant rocking of a sample of **4** in a sealed tube at room temperature for 4 days resulted in a sharp increase in viscosity. Analysis of the reaction mixture by using ^{31}P NMR spectroscopy indicated the presence of an equal mixture of **4** and **5**. This mixture was allowed to react with NaOPh–Ph-*m* as described for polymer **9** in the Experimental Section. The molecular structure of the product (**9**) was confirmed analytically, but GPC analysis showed it to be of low molecular weight ($M_w = 4.5 \times 10^4$, $M_n = 9.8 \times 10^3$).

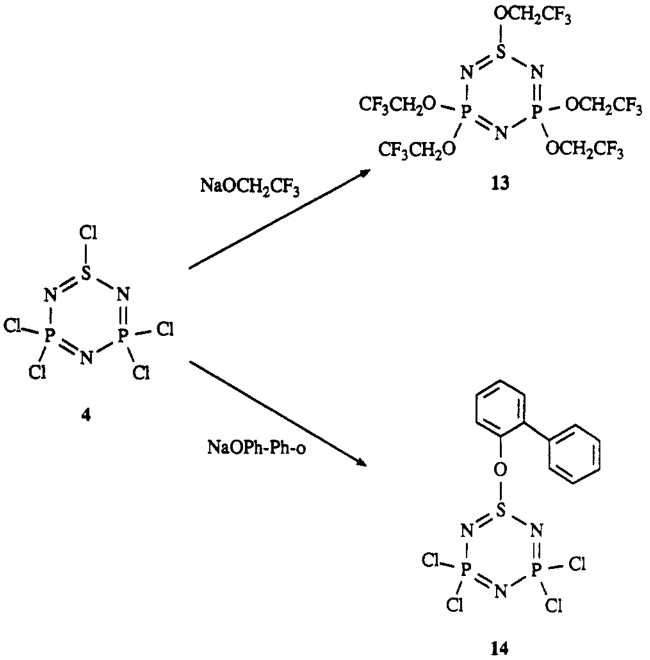
Synthesis of Small-Molecule Cyclic Thiophosphazenes 13 and 14. The following experiments were model reactions designed to assist in the development of the macromolecular chemistry.[10]

Compound **4** reacted in solution with excess sodium trifluoroethoxide to give cyclic trimer **13** (Scheme VI). The product was isolated as an air- and moisture-sensitive oil following solvent extraction. The ^{31}P NMR spectrum of the material consisted of a singlet resonance at 10.5 ppm. Further evidence for the molecular structure was obtained by using high-field ^1H and ^{13}C NMR, elemental microanalysis, and mass spectral analysis.

Scheme V



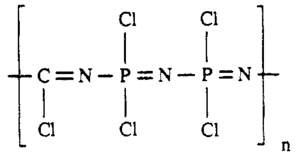
Scheme VI



The higher reactivity of the S–Cl bond in **4** was utilized to prepare a cosubstituent species. Slow addition of a solution of 1 equiv of NaOPh–Ph-*o* to a solution of **4** gave exclusive substitution at sulfur (Scheme VI). The product, **14**, was isolated as a pale green oil by using solvent extraction. The ^{31}P NMR spectrum of **14** consists of a sharp singlet resonance at 19.9 ppm. This shift is only slightly upfield compared to that of **4**, as is expected for substitution at sulfur. Further evidence for the molecular structure was obtained by ^1H and ^{13}C NMR, elemental microanalysis, and mass spectral analysis.

Thermal Transition Behavior of 5, 8–10, and 12. Any comparison of the glass transition temperatures of poly(thiophosphazenes) with classical phosphazenes and poly(carbophosphazenes) must take into account the following factors. First, the introduction of sulfur or carbon atoms into the phosphorus–nitrogen backbone might be expected to change the skeletal flexibility of the individual macromolecules. Second, the thio- and carbophosphazene polymers possess only five side groups per six skeletal atom repeat units, compared to six side groups for the corresponding classical phosphazene.

The T_g values for the chloro derivatives $[NPCl_2]_n$ (**2**), $[N_3P_2SCl_5]_n$ (**5**), and $[N_3P_2CCl_5]_n$ (**15**) provide the simplest comparison, because these polymers bear only chlorine atoms as side units. The T_g values for these polymers are



$$\left[\underset{\displaystyle Cl}{C}{=}N{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}{=}N{-}\overset{\displaystyle Cl}{\underset{\displaystyle Cl}{P}}{=}N \right]_n$$

15

−63,[3] −40, and −21 °C,[4a] respectively. Thus, thiophosphazene **5** has a T_g that is intermediate between those of **2** and **15**. This can be rationalized in terms of the nature of the sulfur–nitrogen multiple bond. The P–N bond in phosphazene compounds is believed to be of the d_π–p_π type, while the C–N bond in carbophosphazenes is a p_π–p_π structure. The barrier to rotation may be much lower in classical phosphazenes than in carbophosphazenes because five 3d orbitals are available for interaction with the $2p_z$ orbital at nitrogen as the P–N bond undergoes 360° torsion. The same may be true for the S–N bond in thiophosphazenes, and this is consistent with the lower T_g value of **5** compared to **15**. No obvious explanation exists for the higher T_g of **5** than **2**. The sulfur–nitrogen bond lengths in cyclothiophosphazenes (ca. 1.56 Å)[11] are similar to the P–N bond lengths in classical phosphazenes (ca. 1.58 Å).[3] This difference is probably not sufficient to influence the skeletal mobility of poly(thiophosphazenes) relative to classical polyphosphazenes. It should be noted that the relationship between skeletal flexibility and T_g is not necessarily a direct one but may represent an indirect influence on the materials free volume.

Polymers **8**–**10** are partially substituted and contain significant amounts of unreacted P–Cl bonds. This factor complicates any comparison of their T_g values with those of classical polyphosphazene analogues.[12] The glass transition temperatures of **8**–**10** are 79, 32, and 69 °C, respectively. The classical phosphazene polymers with the same side groups have T_g values of 67 °C (for $[NP(OPh\text{–}Ph\text{-}o)_{1.52}Cl_{0.48}]_n$), 37 °C (for $[NP(OPh\text{–}Ph\text{-}m)_2]_n$), and 93 °C (for $[NP(OPh\text{–}Ph\text{-}p)_2]_n$).[9] The lower transition temperatures for **9** and **10** might be due to the smaller number of side groups per repeat unit in the thiophosphazenes and to the significant number of chlorine atoms present along the polymer backbone. Both factors may increase the free volume and limit steric repulsions between the bulky aryloxy side groups. In addition, the presence of only five side groups per repeat unit decreases the effective symmetry of the polymers. All these contributions may result in lower T_g values compared to the fully-substituted classical phosphazene analogues.

Cosubstituent polymer **12** has a T_g of 54 °C. This value is lower than that of *p*-phenylphenoxy polymer **10** (T_g = 69 °C). Addition of the second type of side group would be expected to decrease molecular symmetry, thereby increasing free volume and lowering the glass transition temperature of the polymer. However, the T_g of polymer **12** is also lower than that of its closest classical polyphosphazene analogue, $[NP(OPh\text{–}Ph\text{-}p)_{1.5}(OPh\text{–}{}^tBu\text{-}p)_{0.5}]_n$ (T_g = 68 °C).[9] This observation is consistent with those comparisons discussed above for polymers **9** and **10**. Thus, the larger free volume of partially-substituted polymer **12** probably overrides the effect of a slightly less flexible thiophosphazene backbone, giving rise to a T_g that is lower than that of the classical phosphazene analogue.

However, the T_g of polymer **8** (79 °C) is higher than for the classical phosphazene, $[NP(OPh\text{–}Ph\text{-}o)_{1.52}Cl_{0.48}]_n$ (67 °C). Because the degree of aryloxy substitution is similar in each polymer, slight differences in backbone mobility, intramolecular interaction, or free volume may be responsible for the differences.

It is clear from these results that the introduction of sulfur atoms into a phosphorus–nitrogen chain offers new opportunities for probing the relationships between molecular structure and solid-state properties, and these correlations will be the subject of future studies.

Experimental Section

Materials. Compounds **6**[13] and **7**[14] were prepared as reported elsewhere. All phenols were obtained from Aldrich and were purified by sublimation before use. Sodium (Aldrich) was used as received. Trifluoroethanol, hexanes, *n*-heptane, and dichloromethane were distilled from CaH_2 under nitrogen. Dioxane (Aldrich, anhydrous) was distilled from sodium benzophenone ketyl. All reactions and manipulations were carried out under inert atmospheres using either a drybox, glovebag, or standard Schlenk techniques. *All reactants and intermediate products in this work are air- and moisture sensitive, and suitable precautions should be taken.*

Equipment and Techniques. Polymerization experiments were conducted by sealing samples in thick-walled Pyrex tubes (ca. 0.5 × 5 cm) under high vacuum (0.002 mmHg). The tubes were cleaned by soaking overnight in concentrated KOH/2-propanol, rinsing in distilled/deionized water, and then drying overnight at 125 °C. Flame drying and acid neutralization of the tubes both tended to inhibit the polymerization of **4**. All experiments were conducted using thermoregulated ovens that were equipped with mechanical rocking devices to provide continuous tube agitation. NMR spectra were recorded for $CDCl_3$ (^1H and ^{13}C) or dioxane (^{31}P) solutions using either a JEOL FX-90Q or a Bruker WM-360 NMR spectrometer. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or internal $CHCl_3$ (^1H and ^{13}C). Glass transition temperatures were determined with the use of a Perkin-Elmer DSC 7 instrument. Sample weights were between 8 and 11 mg. The samples were heated initially to 115 °C to remove residual solvent and were then rapidly cooled to 0 °C. Measurements were taken at a heating rate of 20°/min. Polymer molecular weights were estimated by means of a Hewlett-Packard 1090 liquid chromatograph equipped with a Hewlett-Packard 1037A refractive index detector. A calibration curve was established using polystyrene standards. Fractionated samples of poly[bis(trifluoroethoxy)phosphazene] of known molecular weight averages (as determined by light scattering and membrane osmometry) were provided by Drs. R. Singler, M. Sennett, and G. Hagnauer (Army Materials Technology Laboratory, Watertown, MA) and were used as controls for our GPC work. Satisfactory agreement was obtained between the polystyrene calibration curve and the poly[bis(trifluoroethoxy)phosphazene] controls. Polymer samples were prepared at a concentration of 0.1% w/w and were eluted with a 0.1% w/w solution of tetra-*n*-butylammonium bromide in tetrahydrofuran through Polymer Laboratories PLgel columns (10^6, 10^6, 10^4-Å pore sizes, 10-μm particle size). Elemental analyses were obtained by Galbraith Laboratories, Knoxville, TN. Mass spectral data were obtained by using a Kratos MS-9/50 (electron impact) or a Kratos MS-50 (fast atom bombardment) instrument.

Synthesis of $N_3P_2SCl_5$ (4). To a suspension of **6** (9.6 g, 29.6 mmol) in CH_2Cl_2 (50 mL) at 0 °C was slowly added a solution of **7** (6.09 g, 29.6 mmol) in CH_2Cl_2 (15 mL). The mixture was warmed slowly to room temperature and was then stirred overnight. The solvent was removed by using an oil pump vacuum, and the resultant pale green oil was transferred to a small distillation apparatus equipped with a short-path distillation head. The apparatus was evacuated (0.002 mmHg), and the flask was then dipped into an 85 °C oil bath.[15] Under these conditions, 4 distills at 72 °C as a very pale green oil. The product was stored at low temperature (–20 °C) to avoid polymerization. Yield: 40–60%.

For 4: ^{31}P NMR (CH_2Cl_2) 24.5 ppm. MS, *m*/*e*: calc 313; found (EI) 278 $(M - Cl)^+$ (100%). See also ref 5.

Synthesis of $[N_3P_2SCl_5]_n$ (5). A sample of 4 (3.0 g, 9.6 mmol) was sealed under vacuum in a Pyrex tube and was then heated at 90 °C.[6] The tube contents gradually increased in viscosity until, after approximately 4 h, the mixture was nearly immobile. (If the viscosity of the product mixture rises to the point that the material no longer flows, it is an indication that cross-linking has occurred, and the material will no longer dissolve in organic solvents.) The tube was broken open in a glove bag and the contents were dissolved in dioxane (30 mL). The solution was filtered to remove glass, and *n*-heptane was added slowly. Amber, elastomeric 5 precipitated from solution. This reprecipitation process was repeated (2×) until no unreacted 4 could be detected by using ^{31}P NMR analysis. Yield: 0.95 g (32%).

For 5: ^{31}P NMR (dioxane) –4.4 (s) ppm. Anal. Calc: Cl, 56.58; P, 19.79; N, 13.41; S, 10.22. Found: Cl, 55.26; P, 19.77; N, 13.80; S, 9.44. DSC: $T_g = -40$ °C.

It should be noted that the polymerization of 4 depends on the history of the sample. Freshly distilled samples of 4 are nearly colorless and may require several days of heating at 90 °C to bring about polymerization. On the other hand, samples of 4 that have been allowed to stand at room temperature overnight become yellow in color and polymerize within 4–5 h when heated at 90 °C.

CAUTION. Attempts to carry out the polymerization reaction at temperatures above 130 °C can generate dangerously high pressures within the sealed glass tube due to the formation of extrusion products (see ref 6).

Synthesis of $[N_3P_2S(OPh\text{–}Ph\text{-}o)_{3.25}Cl_{1.75}]_n$ (8). A solution of NaOPh–Ph-*o* was prepared by reacting *o*-phenylphenol (12.2 g, 71.8 mmol) with excess Na (1.98 g, 86.2 mmol) in dioxane (125 mL). This solution was added dropwise through a fritted filter funnel to a stirred mixture of 4 and 5 (3.0 g, 9.6 mmol, as obtained directly from the polymerization of 4) in dioxane (125 mL) at 12 °C. After the solution had been allowed to react at room temperature for 5 days, the mixture was concentrated to a highly viscous solution by using an oil pump vacuum. This solution was then poured slowly into stirred distilled/deionized water. White, polymeric 8 precipitated from solution. The product was further purified by additional reprecipitations from dry dioxane into water (2×) and into hexanes (3×). Extreme care was taken to allow minimum contact of the material with water. The product was thoroughly dried under vacuum after each precipitation to remove traces of water. Yield: 1.5 g (21%).

For 8: ^{31}P NMR –12.3 and –16.9 (both br, s) ppm; ^{1}H NMR 7.2 (br, s) ppm. Anal. Calc for $[N_3P_2S(OPh\text{–}Ph\text{-}o)_{3.25}Cl_{1.75}]_n$: C, 62.61; H, 3.95; N, 5.62; S, 4.28; Cl, 8.29. Found: C, 61.40; H, 3.85; N, 4.53; S, 3.62; Cl, 7.61. GPC: $M_w = 3.1 \times 10^5$, $M_n = 1.0 \times 10^5$. DSC: $T_g = 79$ °C.

Synthesis of $[N_3P_2S(OPh\text{–}Ph\text{-}m)_{4.4}Cl_{0.6}]_n$ (9). A mixture of 4 and 5 (3.0 g, 9.6 mmol) in dioxane (150 mL) was cooled to 12 °C, and a solution of NaOPh–Ph-*m* (71.8 mmol, prepared as above) was added slowly through a fritted filter funnel. After the reaction mixture had been stirred at room temperature for 3 days, the solution was concentrated using an oil pump and the product was isolated by reprecipitations from dry dioxane into water (3×), hexanes (3×), and 2-propanol (1×). Precautions were taken to minimize hydrolysis as described above for 8. Yield: 0.98 g (12%).

For 9: ^{31}P NMR (dioxane) –12.1 (br, s) ppm; ^{1}H NMR 7.3–7.1 (br, s) ppm. Anal. Calc for $[N_3P_2S(OPh\text{–}Ph\text{-}m)_{4.4}Cl_{0.6}]_n$: C, 70.33; H, 4.40; N, 4.66; Cl, 2.36. Found: C, 71.58; H, 4.06; N, 3.45; Cl, 3.17. GPC: $M_w = 1.15 \times 10^5$, $M_n = 8.51 \times 10^4$. DSC: $T_g = 32°$ C.

Synthesis of $[N_3P_2S(OPh\text{–}Ph\text{–}p)_{4.7}Cl_{0.3}]_n$ (10). A solution of NaOPh–Ph-*p* (71.8 mmol, prepared as above) was added slowly through a fritted filter funnel to a stirred mixture of 4 and 5 (3.0 g, 9.6 mmol) in dioxane (125 mL) at 12 °C. After 5 days at room temperature, the white precipitate was allowed to settle to the bottom of the flask. The transparent, amber-colored mother liquor was transferred via cannula to a Schlenk flask under argon. The polymer solution was then concentrated and poured slowly into a stirred mixture of 2-propanol and acetone (9:1). Further purification was achieved by reprecipitation into an acetone/2-propanol mixture (9:1). Yield: 1.57 g (17%).

For 10: ^{31}P NMR (dioxane) –11.0 (s) ppm; ^{1}H NMR 6.8 (br, s) ppm. Anal. Calc for $[N_3P_2S(OPh\text{–}Ph\text{-}p)_{4.7}Cl_{0.3}]_n$: C, 71.93; H, 4.50; N, 4.46; Cl, 1.13. Found: C, 72.30; H, 5.00; N, 4.50; Cl, 1.08. GPC: $M_w = 1.15 \times 10^5$, $M_n = 2.21 \times 10^4$. DSC: $T_g = 69$ °C.

Synthesis of $[N_3P_2S(OPh\text{–}Ph\text{-}p)_{3.6}Cl_{0.4}(OPh\text{–}^tBu\text{-}p)_{1.0}]_n$ (12). A mixture of 4 and 5 (3.0 g, 9.6 mmol) was dissolved in dioxane (150 mL) and cooled to 12 °C. A solution of NaOPh–^{t}Bu-*p* [from Na (0.26 g, 11.5 mmol) and HOPh–^{t}Bu-*p* (1.45 g, 9.6 mmol) in dioxane (50 mL)] was then added dropwise over a 3-h period. ^{31}P NMR analysis showed complete loss of 5 and the formation of a singlet resonance at –7.3 ppm (11). To this solution was added a solution of NaOPh–Ph-*p* (46.0 mmol, prepared as above) dropwise at 12 °C. After 3 days, the product was isolated in a manner similar to that described above for 10. Isolation was achieved by reprecipitations from dry dioxane into 2-propanol (3×) and into a 2:1 mixture of hexanes/acetone (3×). Yield 0.75 g (8.2%).

For 12: ^{31}P NMR (dioxane) –11.2 (s) ppm; ^{1}H NMR 7.2 (br, s), 1.1 (br, s) ppm. Anal. Calc for $[N_3P_2S(OPh\text{–}Ph\text{-}p)_{3.6}Cl_{0.4}\text{-}(OPh\text{–}^tBu\text{-}p)_{1.0}]_n$: C, 70.34; H, 5.00; N, 4.63; Cl, 1.53. Found: C, 71.09; H, 4.68; N, 4.41; Cl, 1.43. GPC: bimodal molecular weight distribution with peaks at 7×10^4 and 4×10^3. DSC: $T_g = 54$ °C.

Room-Temperature Polymerization of 4. A sample of 4 (3.0 g, 9.6 mmol) was sealed under vacuum in a Pyrex tube. The tube was rocked constantly at room temperature until, after 4 days, the contents were nearly immobile. The tube was opened and the highly viscous oil was dissolved in dioxane (30 mL). Analysis of this solution using ^{31}P NMR indicated the presence of unreacted 4 (50%) and 5 (50%). This mixture was treated with NaOPh–Ph-*m* as described above for 9. Following isolation, the material analyzed well for 9, but the molecular weight was low. GPC: $M_w = 4.5 \times 10^4$, $M_n = 9.8 \times 10^3$.

Synthesis of $N_3P_2S(OCH_2CF_3)_5$ (13). A solution of $NaOCH_2CF_3$ was prepared by treatment of $HOCH_2CF_3$ (3.5 g, 35.0 mmol) with Na (0.97 g, 42.0 mmol) in dioxane (60 mL). This solution was added through a fritted addition funnel to a solution of 4 (2.0 g, 6.4 mmol) in dioxane (60 mL). The mixture was stirred for 12 h. The solvent was removed, and the resultant off-white semisolid was extracted with several portions of hexanes. The extracts were combined, and the solvent was removed to give a transparent, pale yellow oil. Yield: 3.2 g (79%).

For 13: ^{31}P NMR ($CDCl_3$) +10.5 (s) ppm; ^{1}H NMR 4.27 (m, 8 H), 4.13 (m, 2 H) ppm; ^{13}C NMR 123.1 (q, $J_{CF} = 277$ Hz), 122.5 (q, $J_{CF} = 277$ Hz), 64.0–62.0 (m) ppm. MS, *m*/*e*: calc 631; found (FAB) 632 $(MH)^+$ (10%), 532 $(M - OCH_2CF_3)^+$ (100%). Anal. Calc: C, 19.03; H, 1.58; N, 6.66. Found: C, 19.54; H, 1.81; N, 7.04.

Synthesis of $N_3P_2S(OPh\text{–}Ph\text{-}o)Cl_4$ (14). A solution of 4 (2.0 g, 6.4 mmol) in dioxane (40 mL) was cooled to 12 °C, and a solution of NaOPh–Ph-*o* (6.4 mmol, prepared as above) was added dropwise over a period of 3 h. ^{31}P NMR analysis of the reaction mixture showed complete loss of 4 and the formation of a new singlet resonance at 19.9 ppm. The solvent was removed under oil pump vacuum and the resultant semisolid was extracted several times using *n*-heptane. The extracts were combined, and the solvent was removed under vacuum to give a viscous, pale green oil. Yield: 1.9 g (67%).

For 14: ^{31}P NMR ($CDCl_3$) +19.9 (s) ppm; ^{1}H NMR 7.6–7.1 (m) ppm; ^{13}C NMR 137.0, 134.7, 131.6, 129.8, 128.4, 127.7, 126.3, 121.4 ppm. Anal. Calc: C, 32.21; H, 2.01; N, 9.40. Found: C, 31.78; H, 2.23; N, 9.32. MS, *m*/*e*: calc 447; found (FAB) 448 $(MH)^+$ (10%), 278 $(M - OPh\text{–}Ph\text{-}o)^+$ (100%).

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References and Notes

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(6) Higher temperatures (to 130 °C) or longer reaction times (up to 1 week) were sometimes required for the polymerization (see Experimental Section). If higher temperatures are used (>130 °C), an extrusion reaction can occur to give classical phosphazenes $[NPCl_2]_3$, $[NPCl_2]_4$, and $[NPCl_2]_n$ (identified by using ^{31}P NMR analysis. See ref 3). This can lead to a dangerously high-pressure buildup in the sealed tube.

(7) Identified by using ^1H and ^{13}C NMR analysis.

(8) Reaction of **5** with piperidine or the sodium salts of trifluoroethanol, phenol, perfluorophenol, 2-methylphenol, 3-methylphenol, and 2,6-diphenylphenol yielded products that could not be isolated due to air and moisture sensitivity. Reactions with amines were particularly difficult because of the hydrophilicity of the resultant side groups.

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(10) Reaction of **4** with sodium aryl oxides provides products of general structure $N_3P_2S(OAr)_5$, as indicated by ^{31}P NMR and mass spectral analyses. Efforts to purify these oils by using column chromatography, distillation and solvent extraction were not successful.

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(15) A significant amount of product is lost during distillation due to thermal polymerization at this temperature. The product yield is lowered further if the oil is slowly heated to the distillation point.

Registry No. **4**, 38595-77-6; **4** (homopolymer), 124942-31-0; **6**, 15610-64-7; **7**, 18156-25-7; **13**, 144514-49-8; **14**, 144514-50-1; $NaOCH_2CF_3$, 420-87-1; NaOPh–Ph-*o*, 132-27-4.