Both of the copolymers were found to be flame retardant under normal atmospheric conditions. Qualitative tests were carried out simply by holding a flame source to the powdered copolymer. Pure vinylbenzyl chloride and styrene polymers readily ignited and sustained a flame, but the copolymers, even when soaked in flammable solvents, would self-extinguish. This behavior can be attributed to the known flame retardency of the phosphazene system.[2,8] Thus we have shown that by copolymerization with a propenylphosphazene with traditional organic monomers, one can produce copolymers with the flame retardent directly attached to the polymer backbone.

Acknowledgment. This work was supported, in part, by the Office of Naval Research.

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Synthesis of Open-Chain Poly(difluorophosphazene) and Its Reactions with Alkoxides, Aryloxides, and Amines[1]

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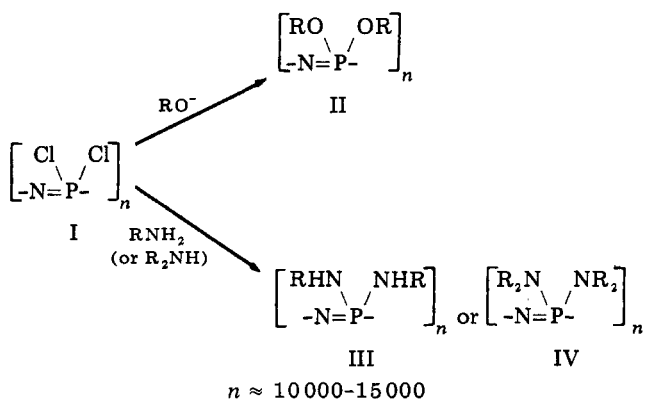
ABSTRACT: The first synthesis of a soluble form of high molecular weight poly(difluorophosphazene), $(NPF_2)_n$, has been carried out, and the reactions of this polymer with amines, alkoxides, or aryloxides have been examined. Poly(difluorophosphazene) reacted smoothly with sodium trifluoroethoxide to yield high molecular weight $[NP(OCH_2CF_3)_2]_n$. However, reactions with amines, such as methylamine, *n*-butylamine, dimethylamine, or aniline, resulted in some chain cleavage and in the formation of nongeminal, partly substituted products of the general formula $[NPF(NHR)]_n$. The limited chain cleavage was ascribed partly to hydrogen fluoride attack on the polymer backbone and also to subsequent hydrolysis of residual P–F bonds. Comparisons with the chemistry of poly(dichlorophosphazene), $(NPCl_2)_n$, indicate fundamental differences between the substitution chemistry of the fluoro- and chlorophosphazene systems, and explanations for these differences are suggested. From a synthetic viewpoint, the unusual reactivity of $(NPF_2)_n$ provides reaction routes to stable new poly(organophosphazenes), such as $[NP(NHC_4H_9)(OCH_2CF_3)]_n$, that are not accessible through $(NPCl_2)_n$.

Poly(organophosphazenes) are some of the most versatile and unusual synthetic macromolecules yet discovered. The first examples were prepared by Allcock, Kugel, and Valan[2-4] by the interaction of soluble poly(dichlorophosphazene) (I) with alkoxides, aryloxides, or amines, and this reaction route has since been used in our laboratory and elsewhere for the synthesis of at least 80 different stable and, in many cases, useful macromolecules.[5-9] The key feature of this reaction route is the use of a highly reactive polymeric intermediate (I) as a precursor for the formation of chemically stable polymeric products (II–IV). An advantage of this route is the large range of poly(organophosphazenes) that can be prepared with the use of the available alcohols, phenols, or primary and secondary amines, both as homopolymers and as mixed substituent derivatives. Thus, the total number of different polymers (with different properties) that can, in principle, be synthesized by this method is comparable to that of all other synthetic macromolecular systems combined.



However, attempts in our laboratory to extend the scope of this field by the reaction of I with organometallic reagents [with a view to the synthesis of polymers of formula $(NPR_2)_n$] led invariably to cleavage of the

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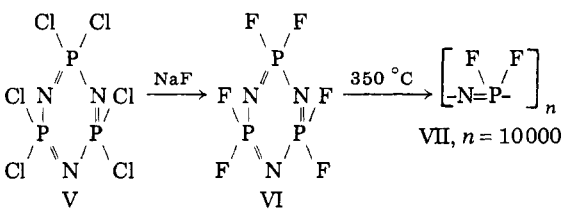
phosphorus–nitrogen chains. It was reasoned that at least part of the sensitivity of I to organometallic reagents was connected with the availability of the lone-pair electrons on skeletal nitrogen for coordination to metal atoms. Hence, the use of poly(difluorophosphazene) (VII) as a reaction substrate offered the prospect that the presence of the more electronegative fluorine atoms might favor halogen replacement at the expense of chain cleavage.

Cross-linked forms of poly(difluorophosphazene) had been prepared previously, but these were unsuitable for substitution reactions because of their insolubility. This paper describes three aspects of the chemistry of poly(difluorophosphazene): (1) a method for the synthesis of uncross-linked, soluble $(NPF_2)_n$, (2) an examination of the reactions of $(NPF_2)_n$ with alkoxides, aryloxides, and amines, and (3) a comparison of the reactions of $(NPF_2)_n$ with those of $(NPCl_2)_n$. The second aspect was a necessary preliminary step for the reactions of $(NPF_2)_n$ with organometallic reagents in order to verify that $(NPF_2)_n$ would indeed participate in nucleophilic substitution reactions in the unusual heterophase solvent systems that must be used. Moreover, it was necessary to confirm that organophosphazene *high* polymers could be generated from $(NPF_2)_n$ with the use of alkoxide or amine reagents that might later be used as cosubstituents with alkyl or aryl groups.

Results and Discussion

Preparation of Poly(difluorophosphazene) (VII). The reaction sequence employed for the preparation of $(NPF_2)_n$ is illustrated in the conversion of V to VII. The



V VI

preparation of VI from V is a well-known reaction.[10] However, the polymerization of VI to VII has been studied only superficially in the past. The samples of VII isolated during previous investigations were amber colored cross-linked elastomers that were swelled by but did not dissolve in fluorinated solvents.[11,12] The polymerization of V to $(NPCl_2)_n$ (I) similarly yields cross-linked polymers unless a careful control of the reaction time, temperature, and reactant purity can be guaranteed.[2,3] Hence, it was surmised that the polymerization of $(NPF_2)_3$ might also be extremely sensitive to the reaction conditions employed.

At 350 °C in a pressurized autoclave (see Experimental Section), the polymerization of $(NPF_2)_3$ passed through three clearly separate stages, from unchanged molten cyclic trimer, through mixtures of trimer with uncross-linked $(NPF_2)_n$, to cross-linked, insoluble $(NPF_2)_n$. Thus, the isolation of $(NPF_2)_n$ in a form that is suitable for substitution experiments requires that the polymerization must be terminated during the second stage.

Experimentally, this is a challenging requirement, because the rate of polymerization of $(NPF_2)_3$ varies dramatically with minor nuances of its history. For example, even a brief exposure of $(NPF_2)_3$ to the atmosphere before polymerization resulted in a much accelerated polymerization. This is in spite of the fact that $(NPF_2)_3$ is generally considered to be moderately stable to atmospheric hydrolysis. Thus, purification of $(NPF_2)_3$ and its transfer to the glass polymerization tubes were carried out within a glass, high-vacuum system. Moreover, rigorous purification techniques were employed for $(NPF_2)_3$. Even so, successive trimer samples vaporized from the same reservoir into polymerization tubes polymerized at progressively slower rates. Under average circumstances, a 40% yield of colorless, soluble $(NPF_2)_n$ could be isolated after 12–14 h at 350 °C, with the remaining 60% of the reaction mixture being unchanged cyclic trimer.

Properties of Poly(difluorophosphazene). Uncross-linked poly(difluorophosphazene) is a white, elastomeric material which is soluble only in perfluorinated solvents. Perfluorodecalin and perfluoro-2-butyltetrahydrofuran were both found to be suitable solvents, although only the latter medium was used in this present work. The solution behavior depended on the extent of polymerization. Polymers obtained from reactions in which less than 40% of the trimer had polymerized were soluble in the perfluorinated solvents alone. Polymers formed in reactions in which the conversion to polymer was 40–70% swelled but did not dissolve in these solvents until a few percent of dry diethyl ether, tetrahydrofuran, or dibutyl ether were added (the latter two solvents are only slightly miscible with the fluorinated media). The addition of larger amounts of diethyl ether resulted in precipitation of the polymer from the fluorinated medium. Polymers that were formed in reactions in which more than 70% of the trimer was polymerized, or from polymerization reactions with impure trimer, or polymers that had been exposed to atmospheric moisture were insoluble in the perfluorinated solvents even after the addition of aliphatic ethers.

The role played by the ethers in this solubilization process is still not clear. One possibility is that the insolubility is a consequence of the presence of microcrystalline domains that are disrupted by the Lewis base action of the ether.

Mechanism of Polymerization. Water and trace impurities exert a powerful accelerating and cross-linking influence on the polymerization. Hence, even in a rigorously purified system, the possibility exists that SiOH units on the surface of the glass polymerization vessel could serve as initiation sites. In such a case, mechanisms of the type proposed earlier[13] for the polymerization of $(NPCl_2)_3$ would apply.

The ring-opening polymerization of $(NPF_2)_3$ at 350 °C takes place without the formation of detectable amounts of higher cyclic oligomers. ^{31}P NMR spectra of $(NPF_2)_3$–$(NPF_2)_n$ mixtures isolated at different stages in the polymerization showed no evidence that the cyclic tetramer was formed in the process. The trimer, tetramer, and high polymer have chemical shifts relative to 85% H_3PO_4 of +9.4, −17.0, and −23.0 ppm, respectively.[14] Polymerization mixtures isolated at various stages from 1.5 to 94% conversion to polymer showed only a decline in the peak of +9.4 ppm and a concurrent growth in the peak at −23.0 ppm (see Figure 1). No additional peaks were seen that might be attributed to branch points, cross-link sites, or end groups. The absence of a broad cyclic-oligomer-containing polymeric series during polymerization is perhaps a consequence of the fact that true equilibrium-type conditions are not attained because of the need to avoid the cross-linking process. The same appears to be true for the polymerization of $(NPCl_2)_3$. In that system, higher cyclic oligomers are detected only when the cross-linked polymer is heated at high temperatures under distinctly nonequilibrium conditions. Although no evidence has been found that might support such a mechanism, we cannot exclude the possibility that at 350 °C the polymerization of $(NPF_2)_3$ proceeds through the

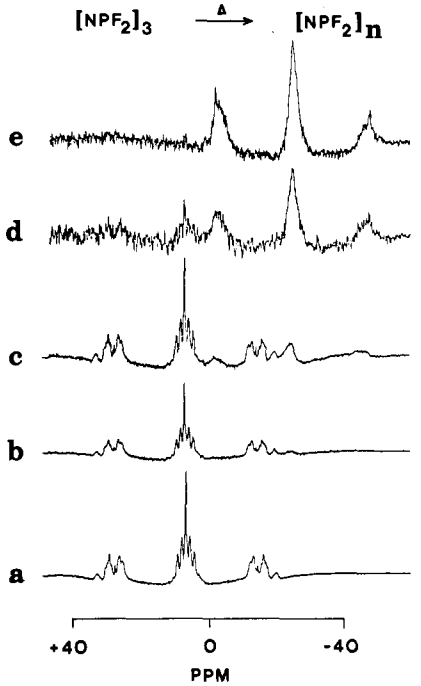


Figure 1. ^{31}P-NMR spectra obtained at different stages during the polymerization of $(NPF_2)_3$ to $(NPF_2)_n$. Spectra a, b, c, d, and e are from samples in which the degrees of conversion to the polymer were 1.5, 5.0, 15.6, 63, and 94%, respectively. The spectra illustrate the disappearance of $(NPF_2)_3$ and the appearance of $(NPF_2)_n$ without the accompanying formation of other species. The spectra were obtained for samples in perfluorobutyltetrahydrofuran solvent and were referenced to an 85% aqueous H_3PO_4 external reference.

transient formation of highly reactive monomer molecules of structure $N{\equiv}PF_2$.

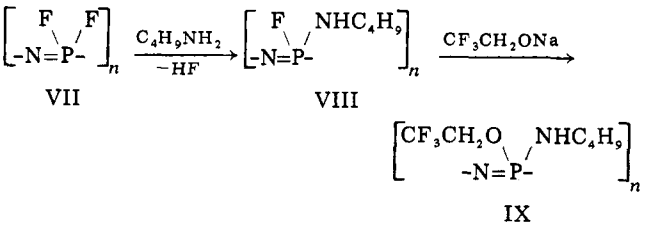
Reactions of $(NPF_2)_n$ with Alkoxides and Phenoxide. The substitution reactions of high polymeric $(NPF_2)_n$ are complicated by the unusual solvent systems that are required. Poly(difluorophosphazene) is soluble only in the perfluorinated solvents, whereas metal alkoxides are insoluble in this medium but are soluble in ethers such as tetrahydrofuran. Hence, heterophase reactions were attempted with these two solvent systems. Under heterophase conditions, $(NPF_2)_n$ reacted with sodium or potassium trifluoroethoxide with apparent replacement of all the P–F bonds to yield polymers of the formula $[NP(OCH_2CF_3)_2]_n$. However, these reactions were slow compared to those of $(NPCl_2)_n$, and the resultant polymers had lower molecular weights (below 500 000). Higher polymers (GPC average mol wt = 2.1×10^6) were isolated when finely divided $(NPF_2)_n$ was first precipitated as a solid from solution in perfluorobutyltetrahydrofuran by the addition of *n*-pentane, followed by the rapid addition of sodium trifluoroethoxide in tetrahydrofuran, removal of the fluorinated solvent and pentane by distillation, and prolonged reaction in boiling ether. The heterophase solution reactions are sufficiently slow that the prospect exists that unreacted P–F bonds will remain. These would then be susceptible to hydrolysis followed by chain cleavage during the purification steps.

The replacement of fluorine in $(NPF_2)_n$ by sodium phenoxide was also a slow reaction, and prolonged reactions in a heterophase solvent system led to replacement of only 90% of the fluorine.

Reactions of $(NPF_2)_n$ with Amines. It is well-known from earlier work that poly(dichlorophosphazene) reacts with many primary or secondary amines with complete replacement of the chlorine atoms by amino residues to yield high molecular weight poly(diaminophosphazenes).[4,15,16] By contrast, poly(difluorophosphazene) underwent only partial substitution by amines such as methylamine, butylamine, aniline, and dimethylamine, and the reactions that did occur were accompanied by some chain cleavage.

For example, $(NPF_2)_n$ reacted with a tenfold excess of *n*-butylamine for 5 days in a heterophase solvent system at 25 °C to yield a polymer of formula VIII.

The structure of VIII was deduced from the ^{31}P NMR



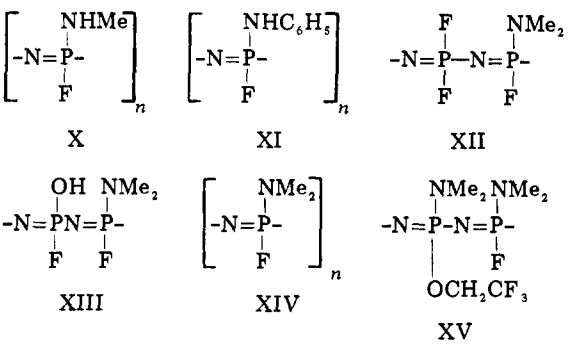
VII VIII IX

spectrum, which showed a complex doublet structure with peak maxima separated by 871.9 Hz.

The presence of unreacted fluorine in these polymers provides a facile route for chain cleavage following even trace hydrolysis to P–OH units. This problem can be avoided by the conversion of VIII to IX by prolonged reaction with sodium trifluoroethoxide, without the isolation or purification of VIII. Polymer IX was hydrolytically stable and had a GPC average molecular weight of 550 000. The nongeminal structure of IX was confirmed by ^{31}P NMR spectra (see Experimental Section).

Similarly, methylamine and aniline reacted with VII to yield the nongeminal substituted products (X and XI). The nongeminal structure was detected from ^{31}P NMR spectra. The occurrence of partial substitution in X strongly suggests that steric hindrance effects are not entirely responsible for this behavior.

However, the reaction of VII with dimethylamine was sensitive to the steric influence of the amine. This reaction was slower than the analogous reaction with aniline. Under mild conditions, less than 50% of the fluorine atoms were replaced by dimethylamino groups (XII). Attempts to



X XI XII

XIII XIV XV

isolate XII led invariably to partial hydrolysis. ^{31}P NMR spectra of the product showed two sets of doublets that were compatible with structure XIII rather than XII. The presence of hydroxyl units was confirmed by infrared spectroscopy. More forcing reaction conditions for the reaction of $(NPF_2)_n$ with dimethylamine yielded the nongeminal substituted product XIV, but subsequent treatment of XIV with sodium trifluoroethoxide removed only part of the remaining fluorine (XV). Thus, the dimethylamino group deactivates the replacement of fluorine both by other dimethylamino groups and by alkoxy groups. Similar effects were reported earlier for the reaction of diethylamine with $(NPCl_2)_n$.[17] Presumably, this phenomenon reflects both a steric shielding effect and an electronic deactivation following electron supply from

dimethylamino toward phosphorus. This would retard further nucleophilic attack at phosphorus. The phenomenon is not entirely a consequence of the low nucleophilicity of dimethylamine, because only partial replacement (84%) of fluorine in VII occurred when the nucleophile was lithium dimethylamide.

The Role of Hydrogen Fluoride. Throughout this work, the suspicion remained that hydrogen fluoride, formed as a reaction product during aminolysis, might cleave the phosphazene skeleton and, hence, contribute to a decline in the chain length of the polymers. Polymer XI, for example, was of lower molecular weight ($\simeq 1 \times 10^4$) than X, and the prospect existed that this was connected with the poor hydrogen fluoride acceptor capability of aniline ($pK_a = 4.6$) and the resultant attack on the chain by free hydrogen fluoride. Similarly, in the reactions of $(NPF_2)_n$ with sodium trifluoroethoxide or sodium phenoxide, free trifluoroethanol or phenol could, in principle, react to generate hydrogen fluoride, which could be soluble in the fluorinated reaction medium.

Cleavage processes of this type are much more likely during the aminolysis reactions of $(NPF_2)_n$ than for $(NPCl_2)_n$ because the salts formed between hydrogen fluoride and amines are known to be weaker than those formed with hydrogen chloride. Thus, an authentic sample of high molecular weight $[NP(NHC_4H_9)_2]_n$ (prepared from poly(dichlorophosphazene))[15] was allowed to react with small amounts of aqueous 5% hydrogen fluoride. The molecular weight declined from 1.2×10^6 to 4.0×10^4. Moreover, the ^{31}P NMR spectrum showed the growth of a new doublet with a peak separation of 1193.3 Hz. This coupling value is consistent with the presence of P–F bonds formed either by butylamine displacement or at the sites of chain cleavage.

However, although the *possibility* of chain cleavage by hydrogen fluoride obviously exists, in practice this is believed to be only a minor contributor to the formation of short-chain products. A more serious factor is the hydrolysis of unreacted P–F bonds during purification of the polymer and during subsequent exposure of the products to the atmosphere.

The possibility also exists that hydrogen fluoride might play a role in the formation of fluoroaminophosphazenes. For example, it is possible that these aminolysis reactions are equilibrium controlled. Amino groups already introduced could perhaps be displaced by hydrogen fluoride. Two items of evidence were obtained that are incompatible with this mechanism. First, lithium dimethylamide yields fluoro(dimethylamino)phosphazenes, even though hydrogen fluoride is absent. Lithium fluoride is insoluble in the reaction medium and cannot participate in amine group displacement. Second, model compound studies between the cyclic $(NPF_2)_4$ and *n*-butylamine carried out in the presence of lithium bromide gave products that were virtually identical to those formed in the absence of this reagent. Any liberated fluoride from hydrogen fluoride should have been removed from the reaction system as insoluble lithium fluoride.[18]

Relationship to the Model Compound Approach. The synthesis and characterization of macromolecules is more difficult and more time consuming than analogous processes carried out with small molecule cyclic analogues. Hence, a motivation exists to perform exploratory mechanistic studies with small molecule systems before attempting the more complex reactions with macromolecules. The results of this present study illustrate that this approach has considerable validity. In another paper, we discussed the reactions of amines, alkoxides, and aryloxides with the cyclic oligomers $(NPF_2)_3$ and $(NPF_2)_4$ and showed that only one fluorine substituent per phosphorus could be replaced by amino residues, although total fluorine replacement occurred with alkoxides and aryloxides.[18] This reaction pattern is also characteristic of the high polymer $(NPF_2)_n$. The cyclic tetramer $(NPF_2)_4$ appears to be an excellent model for the high polymer. Where differences do exist between the cyclic oligomers and the high polymer, they can be ascribed to the different solvent systems required, to the slower reactions of the high polymer (which may be a consequence of chain coiling in solution), and to the high sensitivity of residual P–F bonds in the polymer to hydrolytic attack. The chain-cleavage reactions are detected more readily in the polymeric system because they give rise to severe molecular weight decreases rather than to the simple decrease in yield that would be manifest in a cyclic oligomeric system.

Comparisons between $(NPF_2)_n$ and $(NPCl_2)_n$. First, obvious parallels exist between the syntheses of these polymers from their cyclic trimers. In both cases the ultimate polymerization product is a highly cross-linked elastomer. In both cases also the formation of this ultimate product is preceded by the generation of an uncross-linked linear (or branched) macromolecule. Both reactions are extremely sensitive to the presence of trace impurities and especially to the presence of water. However, the polymerization of $(NPF_2)_3$ does not occur at an appreciable rate at temperatures below ~350 °C, whereas $(NPCl_2)_3$ polymerizes at temperatures above ~240 °C. This may reflect the greater strength of P–F compared to P–Cl bonds if hydrolytic cleavage of the P–halogen bond by traces of water is an important step in the mechanism. Alternatively, the difference may be a consequence of a greater $d\pi$–$p\pi$ stabilization of the ring in $(NPF_2)_3$.

Second, it is clear that the nucleophilic substitution reactions with $(NPF_2)_n$ are more complex than the analogous reactions with $(NPCl_2)_n$. The marked deactivation of the fluorophosphazene polymer as substitution progresses is both a serious problem and an advantage. It is a problem because of the extreme difficulty of preparation of fully substituted aminophosphazene homopolymers from $(NPF_2)_n$ and because of the resultant hydrolytic instability of the partly substituted products. It is an advantage because it provides a facile reaction route to the preparation of nongeminal amino–alkoxy or amino–aryloxy mixed substituent polymers, even when the amino component is methylamine, butylamine, aniline, or dimethylamine. With $(NPCl_2)_n$, these amines react so readily that partial substitution is exceedingly difficult to achieve. The results also show that the use of amines as secondary substituents following, for example, the reactions of $(NPF_2)_n$ with organometallic reagents may lead to incomplete replacement of the remaining fluorine. These reactions of organometallic compounds with $(NPF_2)_n$ will be discussed in a later paper.

Experimental Section

Materials and Analytical Equipment. Hexachlorocyclotriphosphazene (V) (El Monte Chemical Co.) was purified by sublimation, followed by two recrystallizations from heptane. Trifluoroethanol (Halocarbon Products) was dried over molecular sieves. Perfluoro-2-butyltetrahydrofuran and perfluorodecalin (PCR Inc.) were distilled from calcium hydride. Reagent grade tetrahydrofuran (THF) and diethyl ether were distilled from lithium aluminum hydride. Reagent grade acetonitrile, benzene, amines, and hydrocarbons were distilled from calcium hydride.

Gel permeation chromatography was accomplished with the use of a Waters Associates ALG/GPC 501 instrument fitted with a 120 cm × 1 cm 10^6 Styragel column, with tetrahydrofuran used as a solvent. The instrument was calibrated with polystyrene

standards. Hence, the molecular weight values obtained were only approximate. ^{31}P NMR spectra were obtained by means of a JEOL PS-100 FT spectrometer in the FT mode.

Polymerization Equipment. The polymerization reactions were carried out in Pyrex ampules (3 mm wall, 16 mm ID, ~150 mm long, and ~18 mL capacity). Because of the high internal pressures generated within the tubes, heating of the tubes was accomplished within a stainless steel autoclave (21 mm long, 7.5 cm OD, with a central cavity 18 cm long, 3.8 cm ID, with a cap 2.25 cm thick) fitted with a recessed copper gasket and sealed by means of eight bolts in the usual manner. Pressurization was by cyclopentane (65 mL) which has a boiling point (and possibly a critical temperature) similar to that of $(NPF_2)_3$. The tubes were in a vertical configuration. The autoclave was heated to 350 °C in a Freas thermoregulated, gravity convection oven, 2 h being required before the contents of the autoclave reached 350 °C. Thus, the estimated polymerization times were taken as the total heating time minus 2 h. At the end of each experiment, the autoclave was removed from the oven and allowed to cool for at least 4 h before being opened. Rupture of the Pyrex tubes occurred only when more than 15 g of $(NPF_2)_3$ was used. Pressure loss within the autoclave did not occur over 15 h provided that a new, annealed (by heating to cherry red and quenching in water) copper gasket was used for each run. Even so, these polymerizations are potentially hazardous and due precautions should be taken.

Preparation of Soluble Poly(difluorophosphazene) (VII). Hexafluorocyclotriphosphazene (VI) was prepared by the interaction of V with sodium fluoride in acetonitrile.[10] The product was fractionated through a Snyder column, with collection of the center fraction (bp 49 °C). The degassed material was then transferred as a vapor through a Teflon valve into a preconstricted, tared ampule, attached to a vacuum line by means of a Viton A O-ring connector, and cooled in liquid nitrogen. After 12–15 g of $(NPF_2)_3$ had been transferred into the ampule, the ampule was sealed.

After the ampules had been heated in the autoclave at 350 °C and had cooled to 25 °C, they were opened in a dry-nitrogen filled glove bag. The contents were then transferred quickly to a flask, from which unreacted $(NPF_2)_3$ was recovered under vacuum by vapor transfer into a liquid nitrogen cooled tared trap. Either the weight of $(NPF_2)_3$ recovered was used to determine roughly the extent of polymerization, or alternatively, and more commonly, the total polymerization products were transferred to a tared flask, the flask was attached to a vacuum line by means of a Teflon valve adaptor, and the $(NPF_2)_3$ was removed under vacuum during 2 h. The weight of the remaining $(NPF_2)_n$ could then be determined directly.

Solution of the polymer was then effected by the addition of the perfluorinated solvent. The aliphatic ether was added only if solution had not occurred within 24–48 h of agitation at 25 °C. Less than 10% of ether (relative to perfluorinated solvent) was added.

NMR Study of the Polymerization. Thick-walled Pyrex glass ampules (5-g capacity) were attached to a vacuum line by means of ground glass joints and were charged with $(NPF_2)_3$ (1.5–1.7 g). The sealed ampules were heated at 350 °C in the autoclave for 6, 10, 12, 16, and 24 h. After polymerization, homogeneous portions of the tube contents were transferred within a glove bag to NMR tubes that contained perfluorobutyltetrahydrofuran. Those samples which did not dissolve were examined as swollen gels. After the spectra had been obtained, the tube contents and the remaining product were subjected to reduced pressure for 12 h to remove unchanged trimer. The amount of polymer remaining was then determined.

Reaction of $(NPF_2)_n$ with Sodium Trifluoroethoxide. A sample of $(NPF_2)_n$ (3 g, 0.036 mol) was dissolved in freshly distilled perfluorobutyltetrahydrofuran (250 mL) and the polymer was precipitated as a finely divided suspension by the addition of freshly distilled *n*-pentane (50 mL). A solution of sodium trifluoroethoxide, prepared from sodium (8.28 g, 0.36 mol) and trifluoroethanol (43.2 g, 0.432 mol) in THF (250 mL), was added and the polymer dissolved in the tetrahydrofuran phase as the reaction proceeded. Additional THF (250 mL) was added and all of the pentane and most of the fluorinated solvent (total volume, 300 mL) were removed by distillation. This process was repeated by the addition of THF (500 mL) and removal of an additional 300 mL of solvent by distillation. Finally, additional THF (300 mL) was added, and the mixture was boiled at reflux for 48 h. Solvent was removed on a rotary evaporator, and the concentrated residue was precipitated into dilute aqueous hydrochloric acid. Subsequent precipitations from THF into water, hexane, and finally pentane were carried out. The infrared and ^{31}P NMR characteristics of the polymer were identical to those prepared previously from $(NPCl_2)_n$.[2,3] Anal. Calcd for $C_4H_4O_2F_6NP$: C, 19.7; H, 1.65; F, 46.9; N, 5.76; P, 12.75. Found: C, 19.7; H, 1.56; F, 46.7; N, 5.81; P, 12.68. The estimated molecular weight by gel permeation chromatography was 1.1×10^6.

Reaction of $(NPF_2)_n$ with Sodium Phenoxide. A sample of $(NPF_2)_n$ (3.2 g, 0.039 mol) was dissolved in perfluorobutyltetrahydrofuran (250 mL), and dry tetrahydrofuran (20 mL) was then added. A solution of sodium phenoxide, prepared from sodium (8.97 g, 0.39 mol) and phenol (44.0 g, 0.47 mol) in THF (250 mL), was added rapidly and the polymer migrated into the THF phase as the reaction proceeded. The reaction was brought to reflux and was maintained at that temperature for 2 weeks. Solvent was then removed on a rotary evaporator and the concentrated residue was added to dilute aqueous hydrochloric acid. Subsequent precipitations from THF into water or hexane were then carried out.

^{31}P NMR spectra of the product in THF, with the use of a D_2O capillary lock, showed the presence of two sets of bands, a doublet centered at −22.7 ppm (coupling constant 915 Hz) and a singlet at −18.9 ppm. The doublet was assigned to phosphorus atoms that contained one phenoxy and one fluorine pendant group. The singlet arose from phosphorus atoms that contained two phenoxy groups. Integrations of the two areas suggested the presence of 16% residual fluorine atoms.

Reaction of $(NPF_2)_n$ with *n*-Butylamine. This reaction was typical of several carried out between $(NPF_2)_n$ and a number of different amines. A solution was prepared of $(NPF_2)_n$ (3.0 g, 0.36 mol) in perfluorobutyltetrahydrofuran (250 mL). A 1000-mL flask was charged, under dry nitrogen, with dry *n*-butylamine (55 g, 0.75 mol) and THF (500 mL), and the mixture was stirred and cooled to 0 °C. The solution of $(NPF_2)_n$ was then added dropwise during 1 h. After this time the heterophase mixture was allowed to warm to 25 °C and was stirred vigorously for 4 days. The polymer VIII was isolated by addition of the reaction mixture to ether and by repeated solution in chloroform or methylene chloride followed by precipitation into *n*-hexane. In spite of the fact that the polymer contained unreacted P–F bonds, it was not decomposed during a brief exposure to water. The ^{31}P-NMR spectrum in chloroform showed a complex doublet centered at −0.72 ppm, with a coupling constant of 872 Hz. This is in agreement with many P–F coupling values. By contrast, $[PN(NHC_4H_9)_2]_n$ has a ^{31}P chemical shift of +3.48 ppm.

Reaction of $(NPF_2)_n$ with *n*-Butylamine and Sodium Trifluorethoxide. A solution of $(NPF_2)_n$ (3.0 g, 0.035 mol) in perfluorobutyltetrahydrofuran (250 mL) was added dropwise to a stirred solution of *n*-butylamine (30 g, 0.41 mol) in THF (350 mL), and the mixture was stirred at 25 °C for 2 days. The perfluorobutyltetrahydrofuran layer was removed by pipet. It contained no polymer. A 50-mL aliquot of the remaining solution was removed for NMR analysis. In $CDCl_3$ the solute from this aliquot showed a ^{31}P NMR doublet at +1.04 ppm with a coupling constant of 886 Hz. The remainder of the reaction mixture was treated with a solution of sodium trifluoroethoxide prepared from sodium (9.45 g, 0.411 mol) and trifluoroethanol (50 g, 0.5 mol) in THF (100 mL). The reaction mixture was boiled at reflux for 4 days, the solution was concentrated, and the polymer IX was isolated by precipitation in dilute aqueous hydrochloric acid. Purification was effected by several precipitations from THF into water and from THF into hexane. This product in $CDCl_3$ showed a ^{31}P-NMR spectrum that consisted of a singlet at 0.59 ppm, which was compatible with the structure $[NP(NHC_4H_9)(OCH_2CF_3)]_n$. By contrast, $[NP(NHC_4H_9)_2]_n$ in $CDCl_3$ yielded a singlet signal at 3.48 ppm and $[NP(OCH_2CF_3)_2]_n$ in 60:40 THF–acetone showed a singlet at −8.18 ppm. A ^{19}F-NMR spectrum of $[NP(NHC_4H_9)(OCH_2F_3)]_n$ showed a singlet at 38.5 ppm (relative to C_6H_5F) and a doublet at 61.4 ppm with a coupling constant of 879 Hz for $[NPF(NHC_4H_9)]_n$. Chemical analysis of $[NP(NHC_4H_9)(OCH_2CF_3)]_n$ suggested a 60:40 NHC_4H_9–OCH_2CF_3 side

group ratio. Anal. Calcd for $[NP(NHC_4H_9)_{1.2}(OCH_2CF_3)_{0.8}]_n$: C, 36.5; H, 6.5; F, 21.7. Found: C, 37.5; H, 6.4; F, 20.9. Because microanalyses of phosphazenes are known from past experience to be subject to errors, the NMR results are considered to be more reliable.

Reaction of $(NPF_2)_n$ with Methylamine and Sodium Trifluoroethoxide. A Sample of $(NPF_2)_n$ (3.0 g, 0.036 mol) was dissolved in perfluorobutyltetrahydrofuran and was added dropwise to a stirred solution of methylamine (11.2 g, 0.36 mol) in tetrahydrofuran (300 mL). The reaction temperature was maintained at 0 °C until the polymer addition was complete, at which time the reaction mixture was allowed to warm slowly to 25 °C. It was then stirred for 4 days, by which time the product had precipitated from solution. A portion of the precipitated material X was removed, washed with tetrahydrofuran, and dissolved in methanol-d_1. A ^{31}P-NMR spectrum of this sample revealed a doublet centered at 1.09 ppm with a coupling constant of 891 Hz.

The reaction mixture was treated with a solution of sodium trifluoroethoxide prepared from sodium (9.45 g, 0.411 mol) and trifluoroethanol (50 g, 0.5 mol) in THF (100 mL). The mixture was then boiled at reflux for 4 days, the solution was concentrated, and the polymer was washed with a dilute aqueous hydrochloric acid solution. The polymer was subsequently washed several times with water and reprecipitated from THF into water and from THF into hexane. A ^{31}P-NMR spectrum of the product $[NP(NHMe)(OCH_2CF_3)]_n$ showed a sharp singlet at 1.23 ppm (THF). A molecular weight determination (GPC method) suggested an average molecular weight near 1.2×10^6.

Reactions of $(NPF_2)_n$ with Dimethylamine. A solution of $(NPF_2)_n$ (3.3 g, 0.04 mol) in perfluorobutyltetrahydrofuran (250 mL) was added dropwise to a stirred solution of dimethylamine (19.8 g, 0.44 mol) in THF at 0 °C. After the addition was complete, the reaction mixture was stirred at 25 °C for 4 days. A solid product precipitated. A portion of the solid was removed, washed with tetrahydrofuran, and dissolved in methanol. A ^{31}P-NMR spectrum of this product showed two doublets. The large doublet was centered at −1.15 ppm. It showed a coupling value of 897 Hz. The smaller, broader doublet was centered at −6.56 ppm and possessed a coupling value of 830 Hz. The integrated areas showed that the broad band represented 19% of the total peak areas. An infrared spectrum revealed the presence of P–OH bands and, thus, the broad bands were interpreted as resulting from phosphorus atoms which contained pendant hydroxy and fluorine units (XIII).

Reaction of $(NPF_2)_n$ with Dimethylamine and Sodium Trifluoroethoxide. A solution of $(NPF_2)_n$ (3.3 g, 0.04 mol) in perfluorobutyltetrahydrofuran (250 mL) was added dropwise to a stirred solution of dimethylamine (19.8 g, 0.43 mol) in THF at 0 °C. After the addition was complete, the reaction mixture was stirred at 25 °C for 6 days. The reaction mixture was treated with an etheric solution of sodium trifluoroethoxide (9.45 g, 0.411 mol) and trifluoroethanol (50 g, 0.5 mol) in THF (200 mL). The mixture was boiled at reflux for 5 days, the solution was then concentrated, and the polymer was washed with dilute aqueous hydrochloric acid. The polymer was then washed several times with water and was reprecipitated from THF into water and from THF into hexane. A ^{31}P-NMR spectrum revealed a singlet at −0.99 ppm (THF) and a doublet at −1.82 ppm with a coupling constant of 848 Hz. This was indicative of structure XV.

Reaction of $(NPF_2)_n$ with Aniline. A solution of $(NPF_2)_n$ (3.0 g, 0.036 mol) in perfluorobutyltetrahydrofuran (200 mL) was added dropwise to a solution of aniline (67.0 g, 0.72 mol) in tetrahydrofuran (200 mL) at 25 °C. The reaction mixture was stirred at 25 °C for 4 days and then concentrated; the mixture was then added to water. The solid collected was washed several times with benzene and water and was then dissolved in methanol and reprecipitated into water. A ^{31}P-NMR spectrum of the sample in methanol-d_1 showed a doublet centered at −10.2 ppm with a coupling constant of 875 Hz, and this was compatible with structure XI.

Reaction of $(NPF_2)_n$ with Lithium Dimethylamide. Poly(difluorophosphazene) (3.09 g, 0.036 mol) was dissolved in 250 mL of dry perfluorobutyltetrahydrofuran and dry diethyl ether (10 mL). The polymer solution was transferred to an addition funnel and was added dropwise to a tetrahydrofuran solution of $LiNMe_2$ prepared from 25 mL of liquified dimethylamine (0.38 mol) and 0.29 mol of methyllithium (obtained as a 2.05 M commercial solution in diethyl ether). The dark brown reaction mixture was stirred for 48 h and was then concentrated and added to excess water. This procedure yielded a brown, elastomeric solid, which showed a high solution viscosity. Reprecipitation several times from tetrahydrofuran into water and hexane produced a tan solid. A ^{31}P-NMR spectrum of this product (in trifluoroethanol solvent) revealed a singlet at 10.2 ppm (indicative of $P(NMe_2)$ units) and a doublet centered at −2.22 ppm with a coupling constant of 841.5 Hz ($P(F)NMe_2$ units). The integrated areas suggested that the doublet comprised 33% of the total area. Thus, $LiMe_2$ was a better nucleophile toward $(NPF_2)_n$ than was $HNMe_2$. However, even so, complete aminolysis of the polymer still did not occur.

Treatment of Poly(bis(*n*-butylamino)phosphazene) with Hydrogen Fluoride. A sample of $[NP(NHC_4H_9)_2]_n$ in THF was treated with a solution of aqueous 5% hydrofluoric acid in polyethylene vessels at 25 °C for 3 h. The ratio of HF–phosphazene monomer was roughly 1:1. The product was treated with solid sodium carbonate and was subsequently washed with water. The ^{31}P-NMR spectrum of the product dissolved in $CDCl_3$ yielded a singlet at +4.54 ppm and a doublet centered at −4.03 ppm with a coupling constant of 1193 Hz. The doublet comprised 15% of the total peak area. These data suggest that 7.5% of the side groups were fluorine atoms.

Acknowledgment. We thank the Office of Naval Research for the support of this work through Grant No. N00014-75-C-0685. We also thank A. Freyer for his assistance in recording the NMR spectra.

References and Notes

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