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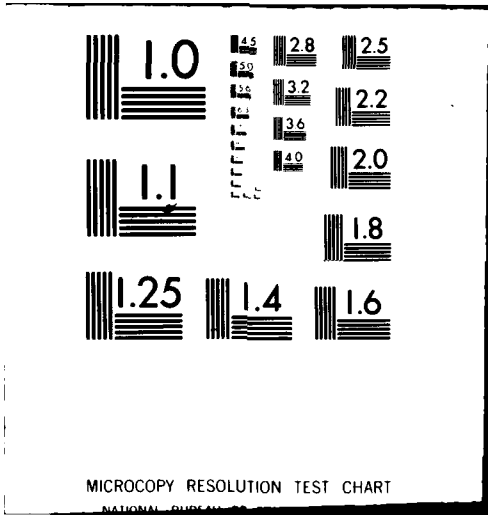
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OF POLY(ORGANOPHOSPHAZENES)**

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T. L. Evans and H. R. Allcock

**Prepared for publication in the Journal
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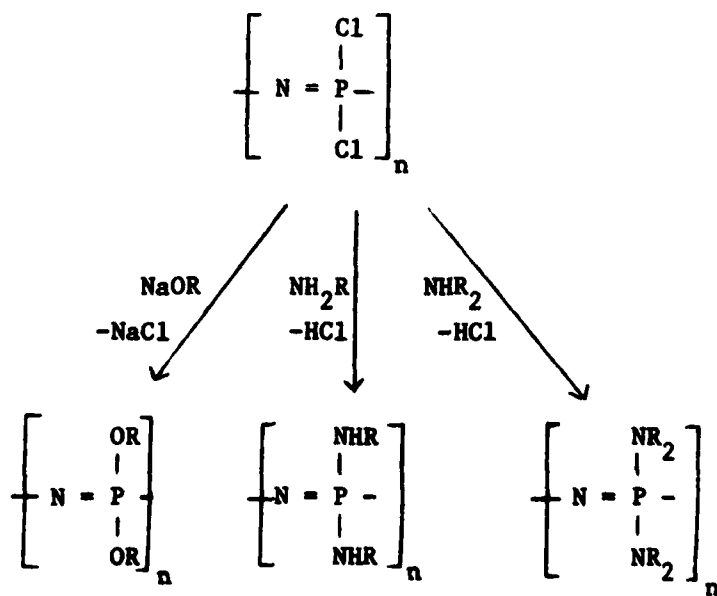
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ABSTRACT

Although many poly(organophosphazenes) have been synthesized, new preparative pathways are needed, especially for polymers that contain alkyl side groups. A new development involves the use of poly(difluorophosphazene), $(NPF_2)_n$, instead of poly(dichlorophosphazene), $(NPCl_2)_n$, as a substrate for reactions with organometallic reagents. This approach has allowed the preparation of a new class of poly(organophosphazenes) that possess substituent groups linked to the skeleton through direct phosphorus-carbon bonds. The synthesis of uncrosslinked poly(difluorophosphazene) and its reactions with alkoxides and amines are also reviewed.

INTRODUCTION

Poly(organophosphazenes) are an unusual and structurally diverse group of inorganic-organic macromolecules that provide valuable chemical and physical differences from conventional organic polymer systems [1, 2, 3]. They are normally prepared by substitution reactions carried out with the highly reactive polymeric intermediate, poly(dichlorophosphazene), $(\text{NPCl}_2)_n$. The well-known interactions of $(\text{NPCl}_2)_n$ with sodium alkoxides, sodium aryloxides, primary amines, or secondary amines have been employed to prepare over 100 polymeric derivatives (Scheme 1). Some of these are of interest as new structural materials or as carrier molecules for chemotherapeutic agents or transition metal species.



R = alkyl or aryl

n = 10,000

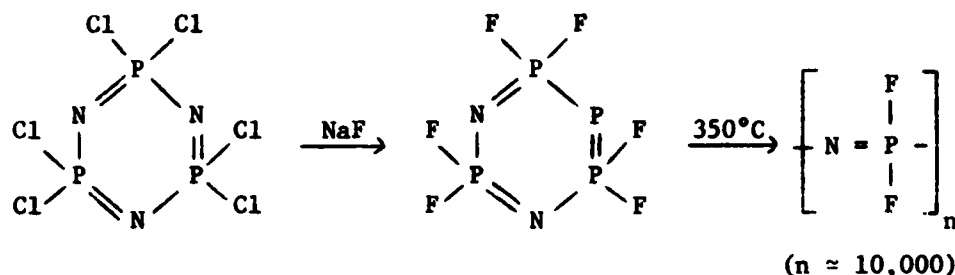
Scheme 1

A major objective in our laboratory over the past 5 years has been to extend Scheme 1 to include the interactions of poly-(dichlorophosphazene) with organometallic reagents with a view to the preparation of poly(alkyl- or arylphosphazenes), $(\text{NPR}_2)_n$. However, the reactions of $(\text{NPCl}_2)_n$ with organolithium or organomagnesium reagents involve concurrent chain scission and substitution reactions. Thus, it has not yet been possible to prepare polymers from $(\text{NPCl}_2)_n$ that possess significant amounts of aryl or alkyl pendent groups without encountering a concurrent molecular weight decline [4].

We have now been able to solve this problem by a new approach which involves the use of poly(difluorophosphazene), $(\text{NPF}_2)_n$, in place of $(\text{NPCl}_2)_n$ [5] as a polymeric reaction substrate. Initially, little was known about the reactions of poly(difluorophosphazene) with simple nucleophiles such as amines or alkoxides. Indeed, until recently, a soluble form of $(\text{NPF}_2)_n$ had not been prepared. Here, we review three aspects of the chemistry of poly(difluorophosphazene): (1) a synthesis route to the preparation of an organic solvent-soluble modification of $(\text{NPF}_2)_n$; (2) the reactions of $(\text{NPF}_2)_n$ with sodium alkoxides, aryloxides, and amines; (3) the reactions of $(\text{NPF}_2)_n$ with organolithium and organomagnesium reagents.

Preparation and Properties of Poly(difluorophosphazene)

A synthesis route to crosslinked poly(difluorophosphazene), $(\text{NPF}_2)_n$, has been known since 1958. However, the crosslinked form is unsuitable for substitution reactions [6]. The first organic-solvent-soluble version of $(\text{NPF}_2)_n$ was prepared in our laboratory in 1974 (Scheme 2).



Scheme 2

This was accomplished by the use of a methodology developed approximately 10 years earlier for the isolation of uncrosslinked poly(dichlorophosphazene). In that earlier work it was found that the crosslinking of poly(dichlorophosphazene) occurs only after 70% or more of the $(\text{NPCl}_2)_3$ has been converted to high polymer. If the polymerization is terminated before this stage, organic solvent-soluble polymer can be isolated [7]. The polymerization of $(\text{NPF}_2)_3$ to $(\text{NPF}_2)_n$ also passes through these same stages, from unchanged molten trimer, through mixtures of trimer with uncrosslinked $(\text{NPF}_2)_n$, to crosslinked, insoluble $(\text{NPF}_2)_n$. Thus, the isolation of poly(difluorophosphazene) in a form that is suitable for substitution experiments requires that the polymerization be terminated during the second stage (70% conversion was the upper limit for the isolation of soluble polymer) [8].

The mechanism of polymerization of trimeric halophosphazenes to poly(halophosphazenes) has not yet been firmly established. However, a ^{31}P NMR study of the conversion of $(\text{NPF}_2)_3$ to $(\text{NPF}_2)_n$ has suggested that no appreciable equilibration between $(\text{NPF}_2)_3$ and $(\text{NPF}_2)_4$ is involved in the polymerization process (Figure 1).

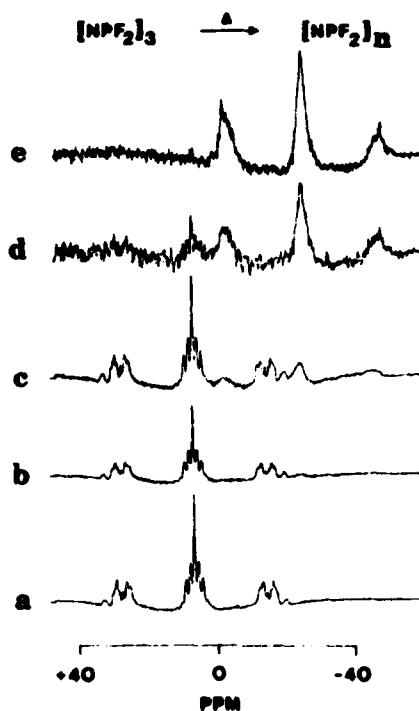


FIG 1. ^{31}P NMR spectra obtained at different stages during the polymerization of $(\text{NPF}_2)_3$ to $(\text{NPF}_2)_n$. Spectra a, b, c, d, and e are from samples in which the degrees of conversion to the polymer were 1.5%, 5.0%, 15.6%, 63%, and 94%, respectively. The spectra illustrate the disappearance of $(\text{NPF}_2)_3$ and the appearance of $(\text{NPF}_2)_n$ 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.

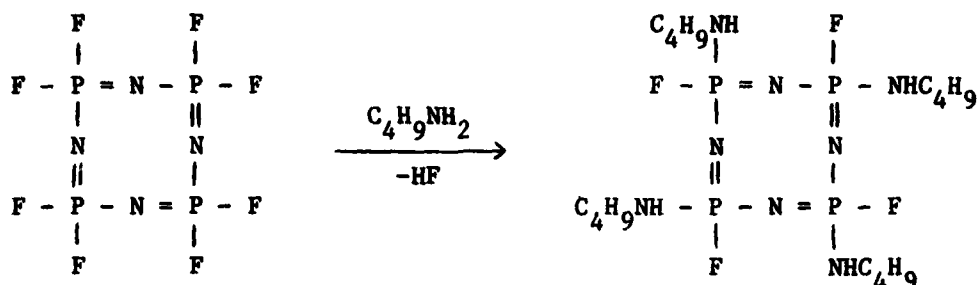
Poly(difluorophosphazene) is a white or colorless elastomeric compound that is hydrolytically unstable and is soluble only in perfluorinated solvents. The unusual solubility behavior of $(\text{NPF}_2)_n$ presented some complications when substitution reactions

were attempted, because the nucleophiles employed in these present studies are soluble in etheric solvents, such as tetrahydrofuran, but are insoluble in perfluorinated solvents. Thus, the substitution reactions described here were carried out in heterophase reaction media.

The Reactions of Poly(difluorophosphazene)

1. Information available from model system studies. The substitution reactions of polymers are often complex. Thus, it is useful to carry out initial mechanistic studies with small molecule model compounds and to utilize the information obtained as a predictive technique for the high polymer reactions [9]. We have employed this method successfully to anticipate the reactions of poly(difluorophosphazene) from studies of the cyclic trimeric and tetrameric model compounds $(\text{NPF}_2)_3$ and $(\text{NPF}_2)_4$. The results of these model studies are as follows.

The reactions of $(\text{NPF}_2)_4$ with sodium trifluoroethoxide or sodium phenoxide resulted in the formation of $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_4$ or $[\text{NP}(\text{OC}_6\text{H}_5)_2]_4$. However, the interactions of $(\text{NPF}_2)_4$ with primary or secondary amines, such as NH_2CH_3 , $\text{NH}_2\text{C}_4\text{H}_9$, or $\text{NH}(\text{CH}_3)_2$, yielded exclusively non-geminally substituted aminofluorophosphazenes. When the same reaction conditions were employed with $(\text{NPCl}_2)_3$, complete amination was accomplished. For example, the reaction of $(\text{NPF}_2)_4$ with an excess of *n*-butylamine yielded $[\text{N}_4\text{P}_4(\text{NHC}_4\text{H}_9)_4\text{F}_4]$ (Scheme 3), but no compounds that possessed higher degrees of amination could be isolated (even at reaction temperatures as high as 60°C). This same substitution pattern was observed for the cyclic trimeric compound $(\text{NPF}_2)_3$, although these reactions were slower than for $(\text{NPF}_2)_4$. However, use of the more reactive reagent, $\text{LiN}(\text{CH}_3)_2$ for reactions with $(\text{NPF}_2)_4$ did yield cyclic compounds such as $[\text{N}_4\text{P}_4(\text{N}(\text{CH}_3)_2)_7\text{F}]$ and $[\text{NP}(\text{N}(\text{CH}_3)_2)_2]_4$ [10] (Scheme 3).



Scheme 3

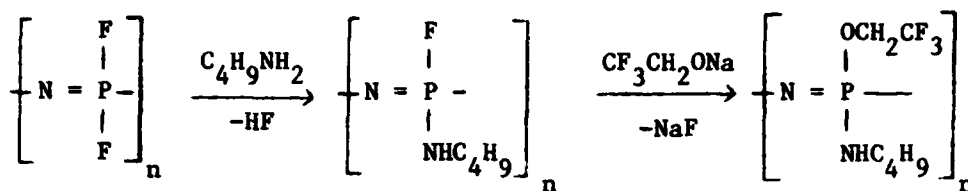
The reaction mechanism for the amination of fluorocyclophosphazenes is still not completely understood. However, the inability of compounds such as $\text{N}_4\text{P}_4(\text{NHR})_4\text{F}_4$ and $\text{N}_3\text{P}_3(\text{NHR})_3\text{F}_3$ to undergo further amination is probably a consequence of three factors: (1) Electron donation takes place from a pendent amino substituent to a phosphorus atom. This deactivates that phosphorus atom to further reaction. The presence of the highly electronegative fluorine atom at that site probably enhances electron donation by the amino group compared with the situation when a chlorine atom is present. (2) The low reactivity of P-F bonds to substitution reactions may contribute to this effect. (3) The weak nucleophilic character of amines toward phosphazene phosphorus atoms reduces the overall reactivity. For these reasons, units such as $[\text{P}(\text{F})(\text{NHR})]$ are more deactivated than $[\text{P}(\text{Cl})(\text{NHR})]$ to further aminolysis, and very reactive nitrogen nucleophiles (e.g. $\text{LiN}(\text{CH}_3)_2$) must be employed before all the P-F bonds can be replaced by amino pendent groups.

Investigations of the reactions of the fluorocyclophosphazenes $(\text{NPF}_2)_3$ or $(\text{NPF}_2)_4$ with organometallic reagents such as methyl lithium, *n*-butyllithium, phenyllithium or methylmagnesium chloride have been carried out in several laboratories [11, 12, 13, 14]. It has been found that the fluorocyclophosphazenes are significantly more resistant to chain degradation reactions

than are chlorocyclophosphazenes.

2. The reactions of $(\text{NPF}_2)_n$ with sodium alkoxides, aryloxides, or amines. The reactions of high polymeric $(\text{NPF}_2)_n$ with sodium trifluoroethoxide or sodium phenoxide are considerably slower than those of $(\text{NPCl}_2)_n$ with the same reagents, but complete fluorine replacement can be effected to yield $[\text{NP}(\text{OCH}_2\text{CF}_3)]_n$ or $[\text{NP}(\text{OC}_6\text{H}_5)_2]_n$. The interactions of $(\text{NPF}_2)_n$ with amines such as NH_2CH_3 , $\text{NH}_2\text{C}_4\text{H}_9$, $\text{NH}_2\text{C}_6\text{H}_5$ or $\text{NH}(\text{CH}_3)_2$ resulted exclusively in the formation of products in which each phosphorus atom possessed one fluorine and one amino substituent [8]. The similarity to the cyclic model systems is striking. These results are illustrated in Scheme 4 for the interactions of $(\text{NPF}_2)_n$ with *n*-butylamine. With $(\text{NPCl}_2)_n$, a non-geminal amination pattern has been detected in only one case, and this involved the interactions of $(\text{NPCl}_2)_n$ with the bulky diethylamine. The substitution pattern for the reaction of $(\text{NPF}_2)_n$ with amines is probably not entirely a consequence of steric inhibition because amines with small steric dimensions (e.g. methylamine) also yield fluoro-amino phosphazenes.

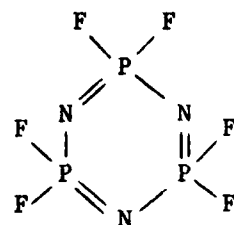
In a practical sense, the partial amination of $(\text{NPF}_2)_n$ is a complicating factor because the residual P-F bonds impart hydrolytic instability to the products. However, it also provides a synthetic advantage for the preparation of new polyphosphazene structures. For example, the reactions of polymers such as $[\text{NP}(\text{NHC}_4\text{H}_9)(\text{F})]_n$ with sodium trifluoroethoxide opens up new synthetic pathways to the formation of polymeric species of the type, $[\text{NP}(\text{NHC}_4\text{H}_9)(\text{OCH}_2\text{CF}_3)]_n$ (Scheme 4). Mixed substituent phosphazenes with the substituent groups arrayed in a regular fashion along the backbone should possess properties that are different from those with the substituents oriented randomly.



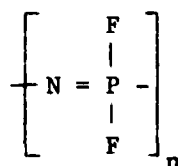
Scheme 4

3. Reactions of $(\text{NPF}_2)_n$ with Phenyllithium. Although poly(difluorophosphazene) is a useful intermediate for the synthesis of alkoxy, aryloxy, or aminophosphazene high polymers, its principle utility is as a substrate for reactions with organometallic reagents to yield species with side groups linked to the skeleton through carbon-phosphorus bonds. Chain cleavage reactions are far less facile when poly(difluorophosphazene) is used as a substrate than when poly(dichlorophosphazene) is employed. This conclusion is based on the studies described in the following sections.

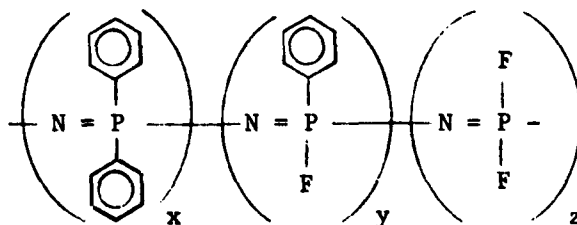
The interactions of $(\text{NPF}_2)_n$ with phenyllithium were carried out as illustrated in Scheme 5. (Sodium trifluoroethoxide was used in most cases as a second nucleophile to ensure complete fluorine replacement). These reactions yielded the first examples of phosphazene high polymers that possess significant percentages of side groups attached to the skeleton through direct P-C bonds [15]. The polymers isolated, their molecular weights and their glass transition temperatures (T_g) are listed in Table 1.



↓ 350°C

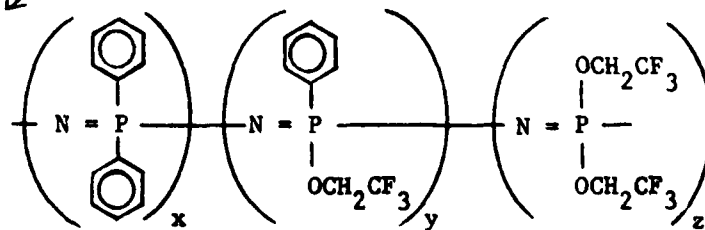
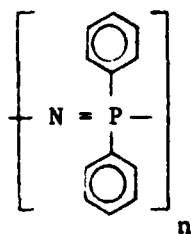


↓ PhLi
-LiF



PhLi
-LiF

NaOCH₂CF₃
-NaF



Scheme 5

TABLE 1. Properties of Poly(alkyl- or arylphosphazenes)

Polymer	GPC M.W. ^a	T _g (°C) ^b
[NP(C ₆ H ₅) _{0.38} (OCH ₂ CF ₃) _{1.62}] _n ^c	> 1 x 10 ⁶	+7
[NP(C ₆ H ₅) _{0.64} (OCH ₂ CF ₃) _{1.36}] _n ^c	> 1 x 10 ⁶	+25
[NP(C ₆ H ₅) _{0.96} (OCH ₂ CF ₃) _{1.04}] _n ^c	> 1 x 10 ⁶	+45
[NP(C ₆ H ₅) _{1.24} (OCH ₂ CF ₃) _{0.76}] _n ^c	> 1 x 10 ⁶	+60
[NP(C ₆ H ₅) ₂] _n ^c	5.0 x 10 ⁴	+70
[NP(CH ₃) _{1.8} (OCH ₂ CF ₃) _{0.2}] _n ^d	crosslinked	-
[NP(CH ₃) _{1.0} (OCH ₂ CF ₃) _{1.0}] _n ^d	crosslinked	-
[NP(C ₄ H ₉) _{0.98} (OCH ₂ CF ₃) _{1.02}] _n ^e	crosslinked	-
[NP(C ₄ H ₉) _{1.5} (OCH ₂ CF ₃) _{0.5}] _n ^e	crosslinked	-
[NP(C ₄ H ₉) ₂] _n ^f	5.0 x 10 ⁴	-45
[NP(C ₂ H ₅) _{1.8} (OCH ₂ CF ₃) _{0.2}] _n ^g	6.0 x 10 ⁵	-60

^a GPC Molecular Weights are relative to polystyrene standards.

^b T_g values were obtained by the torsional pendulum method.

^c Obtained from the interactions of (NPF₂)_n and phenyllithium (at 25°C) followed by treatment with sodium trifluoroethoxide.

^d Obtained from the interactions of (NPF₂)_n and methyllithium (THF; -60°C) followed by treatment with sodium trifluoroethoxide.

^e Obtained from the interactions of (NPF₂)_n and *n*-butyllithium (THF; -60°C) followed by treatment with sodium trifluoroethoxide.

^f Obtained from the interactions of (NPF₂)_n and an excess of *n*-butyllithium (benzene; +2°C).

^g Obtained from the interactions of (NPF₂)_n and diethylmagnesium (THF; 25°C) and then sodium trifluoroethoxide treatment.

The fully phenylated derivatives had lower molecular weights than the mixed-substituent phenyl-trifluoroethoxy polymers. In fact, it was found that approximately 70% of the fluorine atoms could be replaced by phenyl groups before a molecular weight decline was detected. These results are in marked contrast to the rapid molecular weight loss that accompanies substitution during the interactions of phenyllithium with $(\text{NPCl}_2)_n$ [4] (Figure 2).

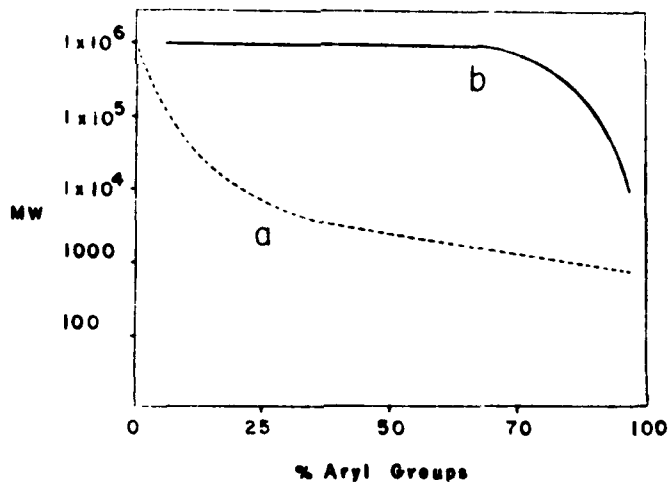


FIG. 2. Comparisons of the variation in GPC average molecular weight for $[\text{NP}(\text{C}_6\text{H}_5)_x(\text{OCH}_2\text{CF}_3)_y]_n$ versus the percentage of phenyl groups attached to the backbone. The broken curve represents the behavior of the system when $(\text{NPCl}_2)_n$ is used as a reaction substrate. The solid line illustrates the behavior with $(\text{NPF}_2)_n$.

An interesting feature of the reaction of $(\text{NPF}_2)_n$ with phenyllithium is the dramatic decrease in reaction rate that occurs after approximately 70% of the fluorine atoms of $(\text{NPF}_2)_n$ have been replaced by phenyl groups. Chain cleavage is encountered during this period of slow substitution. A study of the mechanism of chain cleavage is currently under investigation in our laboratory.

Another interesting feature of the phenylation process is the tendency for phenyl substitution to proceed predominantly, although not exclusively, by a geminal mechanism. This implies that phosphorus atoms that possess one fluorine atom and one phenyl group are more reactive to arylation than are phosphorus atoms that possess two fluorine atoms. This substitution pattern is in contrast to the amination reactions of $(\text{NPF}_2)_n$ described in the previous section. These differences could reflect the higher reactivity of the organolithium reagent than the amines, and possibly the existence of different mechanisms for the two substitution processes.

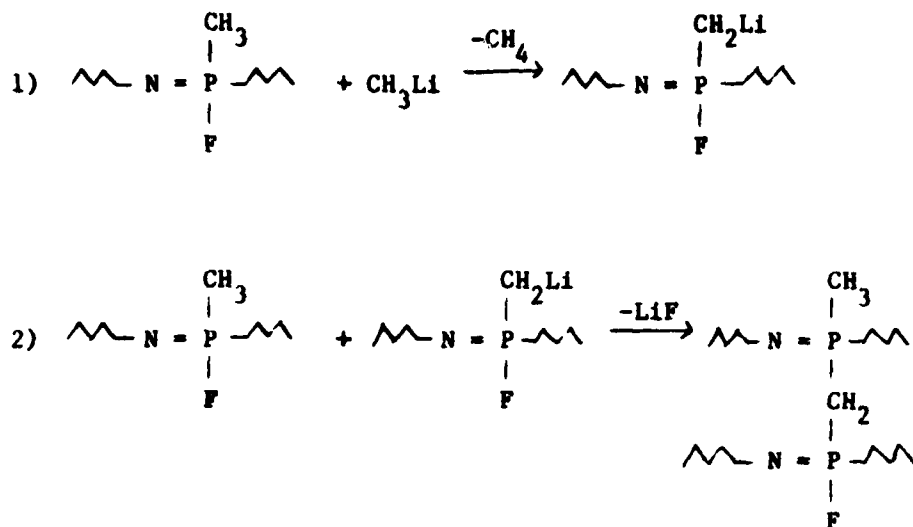
A preliminary study of the thermal behavior of the derivative $[\text{NP}(\text{C}_6\text{H}_5)_{1.32}(\text{OCH}_2\text{CF}_3)_{0.68}]_n$ was carried out. It showed that the presence of the phenyl groups on a polyphosphazene chain increases the stability at 300°C compared with the homopolymer, $[\text{NP}(\text{OCH}_2\text{CF}_3)_2]_n$. Phenyl pendent groups could increase the thermal stability of a polyphosphazene in two ways. First, the low reactivity of a P-C bond as compared with P-O or P-N linkages could reduce the likelihood of side group reactions at high temperatures. Second, the steric bulk of the phenyl group might block the unzipping or backbiting processes that lead to the formation of low molecular weight oligomers.

4. Reactions of $(\text{NPF}_2)_n$ with Alkylolithium Reagents. The interactions of $(\text{NPF}_2)_n$ with methylolithium or *n*-butyllithium are more complicated than those with phenyllithium. With the use of these reagents, crosslinked products were obtained. The cross-

linking process was detected over a wide range of reaction temperatures (for methyllithium from 25°C to -70°C, and for n-butyllithium from 0°C to -70°C). Furthermore, with butyllithium, only low molecular weight products were isolated when the reaction temperature exceeded 0°C. In fact, no reaction conditions were found that did not involve either chain cleavage or crosslinking.

However, it was found that the number of crosslinks per chain decreased as the reaction temperature was lowered. When very low reaction temperatures (-50°C to -70°C) were employed for n-butyllithium or methyllithium, lightly cross-linked products were isolated that possessed high percentages of alkyl pendent groups. These polymers were sufficiently swelled by the reaction media to allow complete fluorine atom replacement to take place with sodium trifluoroethoxide. Some of the polymers prepared in this manner are listed in Table 1.

The crosslinking reaction observed with the use of alkyl-lithium reagents and $(NPF_2)_n$ probably involves two steps: first, proton abstraction from pendent alkyl groups by the alkyl-lithium compound; second, a coupling reaction between the pendent alkyl-lithium substituent from one polymer chain and a phosphorus-fluorine bond from a second polymer chain. This reaction sequence is illustrated in Scheme 6 for the interactions of $(NPF_2)_n$ with methyllithium.



Scheme 6

5. Reactions of $(\text{NPF}_2)_n$ with Organomagnesium Compounds.

The interactions of $(\text{NPF}_2)_n$ with organomagnesium reagents, such as RMgX or MgR_2 yielded mainly crosslinked species. The quantity of organic solvent-soluble products that were isolated from these interactions never exceeded 10%. Even phenylmagnesium bromide or diphenylmagnesium reacted with $(\text{NPF}_2)_n$ to yield crosslinked products. It seems unlikely that proton abstractions from phenyl groups could occur at an appreciable rate at 25°C . Thus, another mechanism for crosslinking, not described by Scheme 6, must be operative with these reagents. Additional research with small molecule model compounds is needed before the mechanistic basis for these reactions can be understood.

ACKNOWLEDGMENT

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