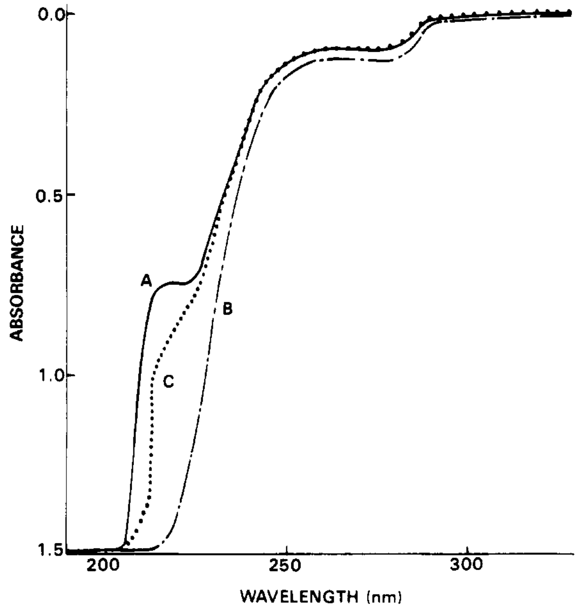

**Figure 2.** Influence of oxygen on ultraviolet absorption spectra: (A) poly(dimethylsiloxane) saturated with $N_2$; (B) poly(dimethylsiloxane) saturated with oxygen; (C) poly(dimethylsiloxane) saturated with air.

Values of $\phi(\mathrm{x, air}) = 0.02$ were obtained for both polymers studied, i.e., of $M_n = 47\,100$ and $M_n = 22\,800$.

In order to estimate a value of $\phi(\mathrm{x})$ for polymers irradiated under vacuum, we used a relative method in which samples were placed in quartz tubes. Because of the large dose required to cause gelation under vacuum, samples were exposed to the more intense medium-pressure lamp. It took longer to gel these samples, relative to ones in quartz tubes open to the atmosphere, by factors of 13 ($M_n = 47\,100$) and 15 ($M_n = 22\,800$). Adopting a value of $\phi(\mathrm{x, air}) = 0.02$ gives an estimate of $\phi(\mathrm{x, vacuum}) = 0.0015$. No other data for poly(dimethylsiloxanes) are known for direct comparison with these values but reference may be made to quantum yields for total gas ($H_2 + CH_4 + C_2H_6$) reported by Siegel and Stewart[19] for wavelengths in the vacuum-ultraviolet region: $\phi(\text{at } 124 \text{ nm}) = 0.136$; $\phi(\text{at } 147 \text{ nm}) = 0.062$. Now for ionizing radiation Miller[15] established the stoichiometric relationship that, approximately, one molecule of gas is formed per cross-link.[20] If this same stoichiometry held also for ultraviolet irradiation, then the present values of $\phi(\mathrm{x, vacuum})$ would appear to be remarkably low. Possibly there is a cage effect[17,18] such that, under vacuum, the quantum yields of both cross-links and total gas decrease with increasing wavelength in the order $\phi(\text{at } 124 \text{ nm}) > \phi(\text{at } 147 \text{ nm}) \gg \phi(\text{at } 254 \text{ nm})$.

In conclusion, from the findings described above and also from other evidence[21] it is inferred that the presence of oxygen during ultraviolet irradiation promotes network formation in polysiloxanes. This is in striking contrast to a retarding effect generally observed in studies of other organic polymers.[22] It is suggested that polysiloxanes are exceptional because of the insensitivity of the backbone to oxidative scission; this brings into predominance cross-link reactions. Further work is needed to elucidate the role of oxygen[23-28] and to identify the chemical structure of the cross-links.[1,29]

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## Cross-Linking Mechanism in the Reactions of Poly(difluorophosphazene) with Alkyllithium Reagents[1]

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Continuing interest exists in the synthesis of poly(organophosphazenes) of formula $(NPR_2)_n$ that contain alkyl or aryl groups linked to skeletal phosphorus via carbon–phosphorus bonds. Such compounds would be analogues of alkyl- or arylsiloxane polymers. Well-developed methods are now available for the synthesis of poly(organophosphazenes) that contain alkoxy, aryloxy, or amino side groups based on the nucleophilic replacement of chlorine in poly(dichlorophosphazene), $(NPCl_2)_n$, by organic residues.[2-6] These methods make use of poly(dichlorophosphazene) as a reactive polymeric intermediate. A logical extension of this approach for the preparation of alkyl or aryl derivatives would involve the reactions of organometallic reagents with a poly(dihalophosphazene).[7]

The reactions of organometallic reagents with halophosphazenes are complex.[8-21] Even so, these interactions are of special interest because of their potential for the synthesis of new high polymeric phosphazenes.[19-21] Earlier work with poly(dichlorophosphazene) has shown that the

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**Table I**
**Properties of Poly[alkyl(trifluoroethoxy)phosphazenes]**

| polymer[a] | reaction conditions | GPC MW[b] | $T_g$,[c] °C |
|---|---|---|---|
| $[NP(CH_3)_{1.8}(OCH_2CF_3)_{0.2}]_n$ | −60 °C (THF) | cross-linked | |
| $[NP(CH_3)_{1.0}(OCH_2CF_3)_{1.0}]_n$ | −60 °C (THF) | cross-linked | |
| $[NP(C_4H_9)_{0.16}(OCH_2CF_3)_{1.84}]_n$ | 0 °C (THF) | $8.1 \times 10^5$ | −57 |
| $[NP(C_4H_9)_{0.30}(OCH_2CF_3)_{1.70}]_n$ | 0 °C (THF) | $5.0 \times 10^5$ | −55 |
| $[NP(C_4H_9)_{0.40}(OCH_2CF_3)_{1.60}]_n$ | 0 °C (THF) | $4.5 \times 10^5$ | −50 |
| $[NP(C_4H_9)_{0.98}(OCH_2CF_3)_{1.02}]_n$ | −60 °C (THF) | cross-linked | |
| $[NP(C_4H_9)_{1.5}(OCH_2CF_3)_{0.5}]_n$ | −60 °C (THF) | cross-linked | |
| $[NP(C_4H_9)_2]_n$ | +2 °C (benzene) | $5.0 \times 10^4$ | −45 |
| $[NP(C_2H_5)_{1.8}(OCH_2CF_3)_{0.2}]_n$ | 25 °C, $Mg(C_2H_5)_2$ (THF) | $6.0 \times 10^5$ | −60 |

[a] Polymer compositions were determined by a combination of $^1H$ NMR and $^{31}P$ NMR methods. [b] Relative to polystyrene standards. [c] By torsional pendulum methods.

**Table II**
**Reaction Conditions for the Preparation of Poly[alkyl(trifluoroethoxy)phosphazenes]**

| polymer prepared | $(NPF_2)_n$,[a,b] g (mol) | RLi, mL (mol) | reaction time, h | reaction temp, °C | Na,[c] g (mol) | $CF_3CH_2OH$, g (mol) | reflux time, h |
|---|---|---|---|---|---|---|---|
| $[NP(CH_3)_{1.8}(OCH_2CF_3)_{0.2}]_n$ | 1.0 (0.012) | 24.1 (0.048) | 18 | −60 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(CH_3)_{1.0}(OCH_2CF_3)_{1.0}]_n$ | 1.0 (0.012) | 24.1 (0.048) | 8 | −60 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(C_4H_9)_{0.98}(OCH_2CF_3)_{1.02}]_n$ | 1.0 (0.012) | 30 (0.048) | 12 | −60 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(C_4H_9)_{1.5}(OCH_2CF_3)_{0.5}]_n$ | 1.0 (0.012) | 30 (0.048) | 18 | −60 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(C_4H_9)_{0.16}(OCH_2CF_3)_{1.84}]_n$ | 1.0 (0.012) | 3.75 (0.006) | 1 | 0 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(C_4H_9)_{0.30}(OCH_2CF_3)_{1.70}]_n$ | 1.0 (0.012) | 7.5 (0.012) | 1 | 0 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(C_4H_9)_{0.4}(OCH_2CF_3)_{1.6}]_n$ | 1.0 (0.012) | 11.3 (0.018) | 1 | 0 | 5.52 (0.24) | 26 (0.26) | 48 |
| $[NP(C_4H_9)_2]_n$[d,e] | 1.0 (0.012) | 30 (0.048) | 1 | +2 | 5.52 (0.24) | 26 (0.26) | 48 |

[a] The polymer was dissolved in PFBT (200 mL). [b] THF (500 mL) was added to the polymer solution before addition of the organolithium unless otherwise noted. [c] The sodium trifluoroethoxide solution was prepared in THF (200–250 mL). [d] The polymer in PFBT (200 mL) was added to the organolithium reagent over the course of 1 h and then the reaction mixture was stirred for 0.5 h. [e] Benzene (500 mL) was used instead of THF in this experiment.

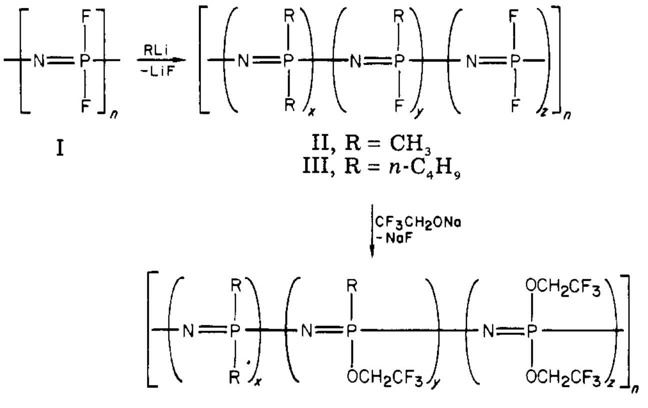
expected halogen-replacement reactions with phenyllithium are accompanied by skeletal cleavage processes.[19] As discussed in this paper, a further complication is encountered when *alkyl* organometallic reagents are used—reactions occur that lead to interchain linkage, and it is of interest to understand the mechanism of this reaction.

Mechanistic questions of this type can often be answered more readily by the use of small-molecule model compounds.[22] However, long-chain macromolecules provide a facile "amplification" process that facilitates the *detection* of molecular linkage reactions, since only a few cross-links per chain bring about insolubilization. Moreover, skeletal cleavage reactions can be monitored readily by the decline in average chain length (assuming that chain cleavage is not paralleled by interchain linkage). Hence, in this work both cyclic model reactants and high polymers were used to investigate the cross-linking process. Poly(di*fluoro*phosphazene) was used as a reaction substrate because of the earlier observations that fluorophosphazenes undergo cleaner reactions with organometallic reagents than do the analogous chlorophosphazenes.[20,21]

## Results and Discussion

**General Characteristics of the Polymeric Reaction.** Two organolithium reagents—methyllithium and *n*-butyllithium—were used for reactions with poly(difluorophosphazene). Poly(difluorophosphazene) is soluble only in perfluorinated solvents such as perfluorobutyltetrahydrofuran (PFBT). For this reason, the reactions were carried out in heterophase reaction media that consisted of $(NPF_2)_n$ in PFBT, with the organolithium reagent dissolved in tetrahydrofuran (THF) or benzene, at temperatures between −70 and +25 °C. After the initial reaction between $(NPF_2)_n$ (I) and the organometallic reagent, the unreacted, hydrolytically unstable P–F bonds were replaced with stable P–$OCH_2CF_3$ units by treatment with sodium trifluoroethoxide. These interactions are summarized in the idealized sequence shown in Scheme I.

Scheme I



I

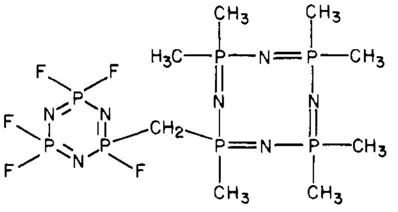
II, R = $CH_3$
III, R = $n$-$C_4H_9$

IV, R = $CH_3$
V, R = $n$-$C_4H_9$

Methyllithium reacted with $(NPF_2)_n$ to bring about both partial replacement of fluorine by methyl and cross-linking. The cross-linking process took place over the temperature range of −70 to +25 °C, although the cross-link density was much less at the lower temperature. Indeed, the polymers formed at −70 to −50 °C swelled sufficiently in THF that they reacted with sodium trifluoroethoxide with virtually total replacement of the remaining P–F units by P–$OCH_2CF_3$. The cross-links were apparently unaffected by this process because the polymers remained highly swollen but insoluble. In the swollen state the lightly cross-linked polymers of type IV gave $^{31}P$ or $^1H$ NMR spectra that were compatible with the side-group ratios 90% methyl/10% trifluoroethoxy or 50% methyl/50% trifluoroethoxy, depending on the reaction conditions employed (Tables I and II).[23]

By contrast, $n$-butyllithium reacted with $(NPF_2)_n$ by a more complicated pattern. At 25 °C, substitution was accompanied by chain cleavage even when a deficiency of the organometallic reagent was present. Typically, the molecular weight (after replacement of residual fluorine by trifluoroethoxy) was less than 10000. However, at lower temperatures the chain-cleavage reaction was accompanied by cross-linking. For example, at 0 °C, in the presence of a deficiency of *n*-butyllithium, more than 90% of the polymer was highly cross-linked, and the remaining 10% (after replacement of fluorine by trifluoroethoxy) was a low molecular weight form of V (Table I). Cross-linking was increased as the ratio of *n*-butyllithium to P–F bonds was increased, and the average molecular weight of the un-cross-linked product was reduced. At –70 to –50 °C the cross-linking reaction was reduced but not totally eliminated. Analysis of such polymers by $^{31}P$ and $^{1}H$ NMR techniques (after replacement of residual fluorine by trifluoroethoxy) in two cases showed side-group ratios of 75% butyl/25% trifluoroethoxy or 49% butyl/51% trifluoroethoxy groups (Table I).[24] Total replacement of fluorine by butyl was accomplished in a PFBT/benzene medium at 2 °C to yield an un-cross-linked polymer of molecular weight $5 \times 10^4$.

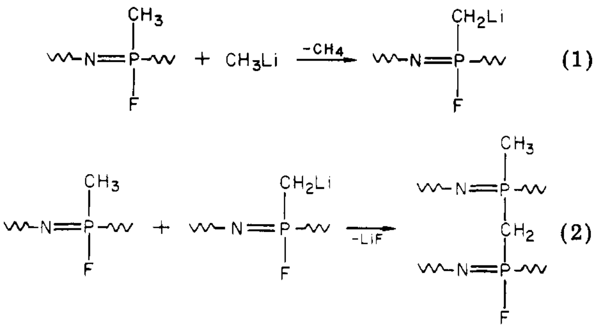
**Small-Molecule Models.** Octamethylcyclotetraphosphazene, $[NP(CH_3)_2]_4$, was treated with 1 equiv of methyllithium at 0 °C in THF solvent. This reaction mixture was added to a THF solution of hexafluorocyclotriphosphazene, $(NPF_2)_3$. Mass spectral analysis of the reaction products indicated the presence of compound VI.[25] This compound is formed by a coupling reaction between $N_4P_4(CH_2Li)(CH_3)_7$ and $(NPF_2)_3$ and is the small-molecule analogue of the high polymeric cross-linked structure. Compound VI was not detected if the same reaction was carried out at –60 °C. However, treatment of $[NP(CH_3)_2]_4$ with methyllithium at –70 °C, followed by treatment with deuterium oxide, yielded the cyclic species $N_4P_4(CH_2D)(CH_3)_7$. Thus, the proton abstraction reaction to yield $N_4P_4(CH_2Li)(CH_3)_7$ is still possible at –60 to –70 °C, but the coupling of this species with $(NPF_2)_3$ appears to be slow at that temperature. This implies that, if the linear polymeric system behaves in a similar manner, metalation is still a facile process at –70 °C, but coupling to another chain is not.


VI

**Cross-Linking Mechanism.** At least one mechanism of cross-linking can be understood in terms of the behavior of the cyclic model species. Cross-linking of II or III appears to involve two steps. First, proton abstraction occurs from the pendent alkyl groups of II or III under the influence of the organolithium reagents, and second, a reaction takes place between the pendent lithioalkyl substituent and a phosphorus–fluorine bond from a second polymer chain. This mechanism is illustrated in Scheme II for the reaction of a methyl-substituted polymer with methyllithium.

**Organomagnesium Reagents.** Substitution and cross-linking also occurs when organomagnesium reagents, such as $C_4H_9MgCl$, $(C_4H_9)_2Mg$, $(C_2H_5)_2Mg$, $C_6H_5MgCl$, or $(C_6H_5)_2Mg$, react with $(NPF_2)_n$ at 25 °C. Un-cross-linked products can be isolated, but these are generally of reduced molecular weight (see Table I and Experimental Section). The halogen-replacement reactions were extremely slow at 25 °C; for example, several days were required for $(C_4H_9)_2Mg$ to replace 70% of the fluorine atoms by butyl groups, whereas the same degree of substitution could be accomplished in 18 h at –60 °C with *n*-butyllithium. At –60 °C the organomagnesium reactions appeared to undergo virtually no reaction (substitution or cross-linking) during 48 h.

Scheme II



In view of the cross-linking mechanism outlined in Scheme II, it is surprising that cross-linking occurs when $(NPF_2)_n$ reacts with *phenyl*magnesium reagents. Metalation of the phenyl groups is unlikely and, moreover, cross-linking does not take place when phenyllithium reacts with $(NPF_2)_n$.[21] Thus, an additional cross-linking mechanism probably exists when organomagnesium reagents react with $(NPF_2)_n$. Coordinative linkage by magnesium atoms to the skeletal nitrogen atoms is a possibility. So, too, are radical-type coupling processes, perhaps catalyzed by transition-metal impurities in the magnesium.[26]

## Experimental Section

**Analytical Equipment.** $^{31}P$ NMR spectra were obtained in the Fourier transform mode at 40 MHz with a JEOL PS-100 FT spectrometer and were processed with a Nicolet 1080 computer (the $^{31}P$ NMR spectra were broad-band $^{1}H$ decoupled). $^{1}H$ NMR data were obtained with the same spectrometer at 100 MHz. Approximate polymer molecular weights were determined with a Waters Associates ALC/GPC 501 instrument fitted with a 120 cm × 1 cm, $10^6$ Styragel column, with tetrahydrofuran as solvent. The instrument was calibrated with polystyrene standards. Glass transition temperatures ($T_g$) were measured with a Chemical Instruments Corp. torsional braid analyzer provided by NASA, Langley Field. Mass spectrometric analyses were obtained with an AEI MS 902 spectrometric instrument.

**Materials.** All experimental manipulations were performed under an atmosphere of dry nitrogen (Matheson). Tetrahydrofuran (THF) (Fisher) and dimethoxyethane (Fisher) were freshly distilled under nitrogen from sodium benzophenone ketyl. Commercial methyllithium (Aldrich, 2.0 M in diethyl ether solvent) and *n*-butyllithium (Foote Mineral, 1.6 M solution in hexane solvent) were used as received. Sodium trifluoroethoxide was prepared from sodium pellets (Matheson Coleman and Bell) and trifluoroethanol (Halocarbon Products) dried over 4-Å molecular sieves. Perfluorobutyltetrahydrofuran (PFBT) (PCR) was used as received. Ethyl bromide, *n*-butyl bromide, and bromobenzene (Aldrich) were distilled before use.

**Synthesis of Poly(difluorophosphazene) (I).** This polymer was prepared by the thermal polymerization of hexafluorocyclotriphosphazene, $(NPF_2)_3$, at 350 °C in sealed tubes by the method described previously.[27] The conversion of the trimer to high polymer was restricted to the range of 40 to 60% to ensure the formation of fluorocarbon-soluble polymer. Unreacted trimer was removed under vacuum.

**General Experimental Procedure.** Specific experimental details for the synthesis of poly(alkylphosphazenes) are summarized in Table II. Here, we describe a general experimental procedure. A sample of poly(difluorophosphazene) (I) was dissolved in PFBT, and the THF phase was added. If a reaction was to be carried out at low temperatures, the reaction system was cooled by means of a dry ice–acetone bath (–60 °C) or a water-ice bath (0 °C). The organolithium reagent was then introduced and the reaction mixture was stirred. The organolithium compound was deactivated by the addition of a slight molar excess of trifluoroethanol (if low reaction temperatures were employed, the quench was carried out at low temperature), and a solution of sodium trifluoroethoxide was then added. The reaction mixture was then boiled at reflux for 48 h. Isolation of the polymeric product was accomplished in the following way. The reaction mixture was concentrated by means of a rotary evaporator and the concentrate was added to a dilute aqueous HCl solution. The precipitated polymer was collected by filtration and was washed with water several times. Products that were soluble in organic solvents were purified by reprecipitation from THF into water and from THF or methylene chloride into pentane or hexane.

**Characterization of $[NP(R)_x(OCH_2CF_3)_y]_n$.** The ratios of alkyl to trifluoroethoxy units in the purified products were determined by $^1H$ NMR and $^{31}P$ NMR methods.[28] The percentages of alkyl groups present agreed to within 5% by these two techniques. Polymers with the general formula $[NP(CH_3)_x(OCH_2CF_3)_y]_n$ yielded $^{31}P$ NMR spectra that showed resonances at +15.2, +13.8, and -7.9 ppm.[29] These were assigned, respectively, to phosphorus atoms that possessed two methyl groups, one methyl and one trifluoroethoxy group, and two trifluoroethoxy substituents. The $^1H$ NMR spectra of these polymers consisted of a doublet centered at +2.0 ppm (methyl protons) and a multiplet centered at +5.2 ppm (trifluoroethoxy protons). Polymers with the general structure $[NP(C_4H_9)_x(OCH_2CF_3)_y]_n$ yielded $^{31}P$ NMR spectra that included resonances at +19.1 ppm (broad—$PR_2$ and $P(R)(OCH_2CF_3)$ units) and -8.2 ppm ($P(OCH_2CF_3)_2$ units).[29] $^1H$ NMR spectra of these compounds consisted of resonances at +1.5 ppm (broad—butyl protons) and +5.2 ppm (trifluoroethoxy protons).

**Reactions of $[NP(CH_3)_2]_4$ with $CH_3Li$ Followed by Treatment with $(NPF_2)_3$.** A sample of $[NP(CH_3)_2]_4$ (1.0 g, 0.0033 mol) was dissolved in THF (50 mL), and the solution was cooled to 0 °C by means of a water-ice bath. A solution of methyllithium (1.6 mL, 3.3 mmol) was then added dropwise over the course of 2 min. The reaction mixture was then stirred for 15 min, and a sample of $(NPF_2)_3$ (0.82 g, 3.3 mmol) in THF (10 mL) was added. When the addition was complete, the reaction mixture was stirred for 1 h. The reaction mixture was then evaporated to dryness by means of a rotary evaporator. Any unreacted $(NPF_2)_3$ or $(NPMe_2)_4$ was removed under vacuum. The residue was then dissolved in THF (10 mL) and filtered to remove lithium fluoride, and heptane was added to the filtrate. A solid was collected by filtration. Mass spectrometric analysis of this solid indicated the presence of a compound with the formula $[N_3P_3F_5-CH_2-N_4P_4(CH_3)_7]$ (VI) (*m/e* 529).

A similar reaction sequence performed at -60 °C did not result in the isolation of VI. However, if deuterium oxide was added to a reaction mixture that contained $[NP(CH_3)_2]_4$ and methyllithium at -70 °C, a compound with the formula $[N_4P_4(CH_2D)(CH_3)_7]$ could be isolated. This result suggests that the proton-abstraction process is still possible at reduced temperatures.

**Reactions of $(NPF_2)_n$ with Organomagnesium Reagents.** The interactions of $(NPF_2)_n$ with RMgX or $MgR_2$ (where R = ethyl, butyl or phenyl) resulted in low yields of organic-soluble products, with most of the reaction products being cross-linked. The synthetic procedure employed for the preparation of a polymer with the structure $[NP(C_2H_5)_{1.8}(OCH_2CF_3)_{0.2}]_n$ is described in this section and serves as an example of the general procedures employed.

A solution of $Mg(C_2H_5)_2$ [prepared from magnesium (11 g, 0.45 mol) and ethyl bromide (69.8 g, 0.64 mol) in dimethoxyethane (200 mL) and separated from $MgBr_2$ by filtration] was added at 25 °C to a heterophase reaction mixture that contained $(NPF_2)_n$ (6.1 g, 0.073 mol) in PFBT (250 mL) and THF (700 mL). The reaction mixture was stirred for 48 h (at 25 °C), a slight molar excess of trifluoroethanol was added to deactivate the organomagnesium reagent, and sodium trifluoroethoxide [prepared from sodium (9.0 g, 0.39 mol) and trifluoroethanol (140 g, 1.40 mol) in THF (200 mL)] was added. The reaction mixture was refluxed for 24 h. Separation of the un-cross-linked product from the cross-linked material was effected by filtration of the reaction mixture, followed by treatment of the filtrate with aqueous HCl solution and collection of the precipitated polymeric solid by filtration. Purification of the product involved reprecipitations from THF into water and from THF into pentane (several times). The yield of soluble product was 10% (GPC molecular weight was $6.0 \times 10^5$).

Polymers with the structures $[NP(C_4H_9)_{1.5}(OCH_2CF_3)_{0.5}]_n$, $[NP(C_6H_5)(OCH_2CF_3)]_n$, and $[NP(C_6H_5)_{0.5}(OCH_2CH_3)_{1.5}]_n$ were also prepared in a similar manner from the interactions of $(NPF_2)_n$ with $Mg(C_4H_9)_2$, $Mg(C_6H_5)_2$, or $(C_6H_5)MgCl$. The molecular weights of these products were over $1 \times 10^5$.

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(24) A $^{31}P$ NMR study of this substitution pattern showed that butylation of $(NPF_2)_n$ in the presence of excess *n*-butyllithium proceeded in a predominantly geminal manner. After 6 h at -60 °C the polymeric product possessed 31.5% butyl and 68.5% fluorine substituents. Of these, 27% were $PR_2$, 9% were PRF, and 64% were $PF_2$ units.

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