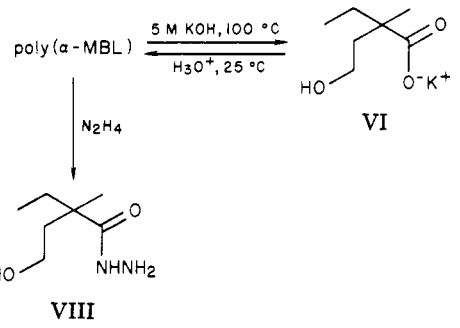
Table III
Some Typical Properties of Poly(α-methylene-γ-butyrolactone) Prepared by Free-Radical Initiation[a]

crystallinity	amorphous
microtacticity	atactic, slightly rich in syndiotactic placements (P_{rr} = 0.43, P_{mr} = 0.44, P_{mm} = 0.13)
T_g, °C	195
thermal stability	major decomposition ≥320 °C; thermally depolymerizes to monomer
solubility	insoluble in most common organic solvents, soluble in DMF and Me_2SO
tensile strength, psi	9100
ultimate elongation, %	6.5
tensile modulus, psi	2.9×10^5

[a] 0.05% AIBN in bulk, η_{inh} = 1.04 (Me_2SO, 25 °C).

slowly hydrolyzed by strong alkali. Treatment with 5 M KOH for several hours at 100 °C gives the highly hydrophilic but water insoluble potassium salt of poly(α-methylene-γ-hydroxybutyric acid) (VI) which showed the characteristic IR band at 1580 cm^{-1} for carboxylate and the absence of lactone carbonyl indicating completion of the saponification. However, the free acid could not be isolated since mere acidification of a suspension of VI in



water at 25 °C caused complete lactonization to poly(α-MBL) as indicated by IR (Figures 2C and 2D). The ready tendency of γ-hydroxybutyric acid to form the lactone is well known[22] and appears to be particularly strong in the case of this polymer. Reaction of poly(α-MBL) with hydrazine, a strong nucleophic base, gave water-soluble poly(α-methylene-γ-hydroxybutyric acid hydrazide) (VII).

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Reaction of Phenyllithium with Poly(dichlorophosphazene)[1]

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ABSTRACT: The reaction between poly(dichlorophosphazene), $(NPCl_2)_n$, and phenyllithium has been studied with changes in temperature, reaction time, media, and mole ratio of reactants and in the presence of chelate complexes. The results showed that the chlorine substitution reaction is a slow process, while chain cleavage is much faster and dominates the overall reaction pattern. The nucleophilic replacement of halogen atoms yields high polymers of formula $N_nP_nCl_xPh_y$ that contain up to 10% phenyl-substituent groups. The remaining chlorine atoms can be replaced by treatment with sodium trifluoroethoxide or *n*-butylamine. The properties and molecular structure of the products are discussed.

This work on the synthesis of aryl-substituted polyphosphazenes is an outgrowth of our earlier synthesis of the first high polymeric phosphazenes that contained amino,[2,3] alkoxy, or aryloxy[4] groups. These were formed by the nucleophilic displacement of chlorine in poly(dichlorophosphazene), $(NPCl_2)_n$ (I), by amines, alkoxides, or aryloxides. We now report the reactions of $(NPCl_2)_n$ with phenyllithium with a view to the replacement of chlorine by phenyl to yield polymers with repeating units, such as II or III.

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$$\left[\text{-N=P(Cl)}_2\text{-}\right]_n \xrightarrow{\text{PhLi}} \sim\!\sim\text{N=P(Ph)(Cl)}\sim\!\sim \xrightarrow{\text{PhLi}}$$

I II

$$\sim\!\sim\text{N=P(Ph)}_2\sim\!\sim$$

III

The phenyl substituent was chosen for this study for three reasons. First, phosphorus–phenyl bonds are known to have a high stability. Second, in contrast to the use of alkyllithium reagents, no complications were expected from α-metallation reactions when phenyllithium was used as a nucleophile. Third, phenyllithium has a higher nucleophilicity and lower electrophilicity than phenylmagnesium bromide or diphenylmagnesium and, hence, would be expected to offer the best prospects for halogen replacement rather than nucleophilic chain cleavage. As will be shown, this latter factor of the ease of substitution vs. chain cleavage is the most critical feature of the reactions of poly(dihalophosphazenes) with organometallic reagents.

Attempts have been made in the past by other investigators to synthesize polymers of this type. For example, the reaction of sodium azide with phenyldichlorophosphine was reported to yield low polymeric phenylchlorophosphazenes[5] with an average molecular weight of about 5000. Earlier attempts to use Grignard or organolithium reagents to replace the halogen in $(NPCl_2)_n$[6,7] resulted in the formation of low molecular weight or cross-linked species of uncertain composition.

It is known that the reactions of cyclic chlorophosphazenes $(NPCl_2)_{3 \text{ and } 4}$ with phenylmagnesium halides, diphenylmagnesium, or phenyllithium involve skeletal cleavage reactions.[8-11] However, the resultant short chain linear oligomers react rapidly with organometallic reagents in a halogen substitution sequence, apparently without appreciable chain cleavage.[8-11] Such interactions can be viewed as model systems for the reactions of high polymeric $(NPCl_2)_n$ with organometallic reagents. As will be demonstrated, the reactions of $(NPCl_2)_n$ with phenyllithium are complex and differ greatly from the remarkably clean interactions of $(NPCl_2)_n$ with alkoxides, aryloxides, or amines.[2-4] Indeed, the interactions of $(NPCl_2)_n$ with organometallic agents are, if anything, more complex than those reported earlier for $(NPF_2)_n$.[12]

Results and Discussion

Relationship between the Degree of Phenylation and the Polymer Chain Length. Both phenylation and chain cleavage occurred when $(NPCl_2)_n$ was allowed to react with phenyllithium. The cleavage process took place even when a molar deficiency of phenyllithium existed in the reaction mixture. Thus, it was of considerable interest to determine if a relationship exists between the degree of phenylation and the extent of chain cleavage. The objective was to find a set of reaction conditions that would lead to the maximum degree of phenylation coupled with an acceptable minimum amount of chain cleavage.

Therefore, a number of reactions were performed in which the reactant ratio of $NPCl_2$ units to phenyllithium was varied from 1:0.3 to 1:1. Experimental problems did not permit the isolation of the partially substituted phenylchlorophosphazene polymers formed in the reaction mixture. These species were found to be hydrolytically unstable and prone to cross-link formation[13] (via hydrolysis of P–Cl to P–OH groups and condensation to P–O–P cross-links) during purification. Hence, before isolation and purification, the reaction products were treated with a second nucleophile (sodium trifluoroethoxide or butylamine) in order to replace the residual chlorine atoms

Scheme I

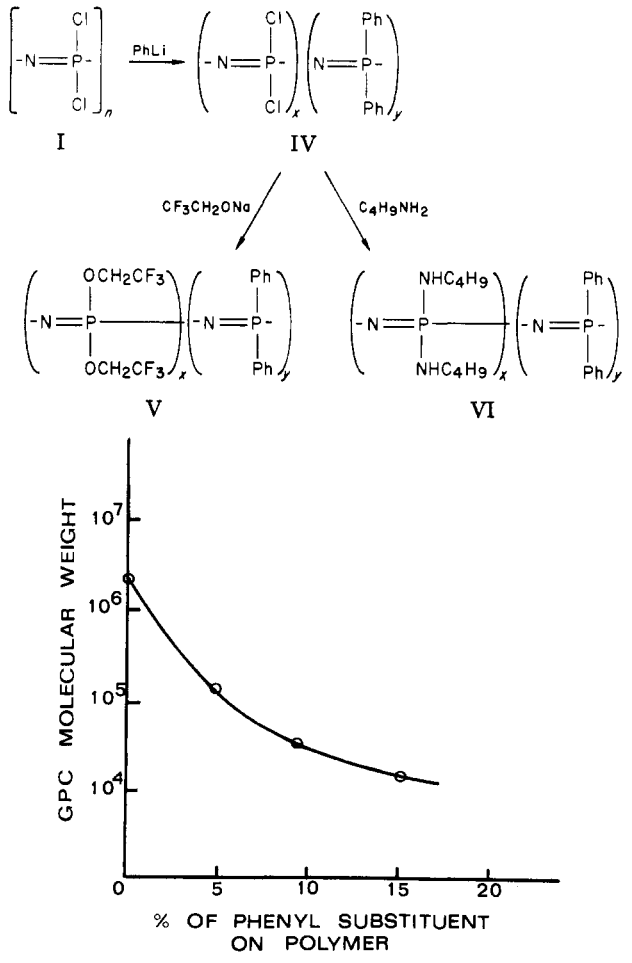


Figure 1. Changes in the GPC molecular weight as a function of the percentage of phenyl substituents in the polymer. The cosubstituent is trifluoroethoxy.

and form hydrolytically stable derivatives. The overall substitution pathway is illustrated in the conversion of I to IV, V, and VI (Scheme I).

The use of this reaction sequence made it necessary to first establish that the chain length was not altered by the subsequent treatment with the alkoxide or the amine. Thus, a control reaction was carried out in which a sample of IV was separated into two portions. One portion was treated with sodium trifluoroethoxide and the other with *n*-butylamine. Gel permeation chromatography showed that the molecular weights of both polymeric products were similar. Hence, based on the widely differing nucleophilicities of these two reagents, it seems unlikely that chain cleavage takes place with the second nucleophile.

The chain length of the polymers decreased rapidly as the ratio of phenyllithium to $NPCl_2$ units in the reaction mixture was increased and as the phenyl group content of the polymer increased. The results are summarized in Table I and Figure 1. Thus, the question must be raised whether phenylation is coincident with or in some way directly connected with chain cleavage.

It was not possible to "uncouple" the cleavage and substitution processes by changes in reaction temperature and solvent or by the use of coordinative additives, such as tetramethylethylenediamine. Thus, the cleavage and substitution processes appear to be coupled either by a mechanistic interaction or by similar activation energies. Some discrimination against chain cleavage was accomplished by the use of $[NP(Cl)(OCH_2CF_3)]_n$ as a substrate in place of $(NPCl_2)_n$. In this case, 20% of the product was

Table I
Analytical Data for $[NP(C_6H_5)_x(OCH_2CF_3)_y]_n$[a]

	% C		% H		% N		% P		% F			
c	calcd	found	calcd	found	calcd	found	calcd	found	calcd	found	T_g, °C	mol wt[b]
0	19.78	19.80	1.65	1.74	5.76	5.84	12.75	12.83	46.90	47.10	−66	3.0×10^6
5	21.95	21.60	1.79	1.85	5.83	5.88	12.86	12.85	44.96	43.03	−58	1.5×10^5
9	23.72	23.04	1.90	2.07	5.86	6.26	12.96	13.62	43.39	39.62	−42	5.0×10^4
15	26.42	25.69	2.07	2.16	5.92	6.14	13.10	13.60	40.98	35.17	−30	3.0×10^4

[a] All polymers contained no residual chlorine (Beilstein test). [b] By gel permeation chromatography in tetrahydrofuran. [c] Percent phenyl groups introduced.

a medium molecular weight polymer (mol wt = 1.0×10^5) in which 20% of the side groups were phenyl units. However, metallation of the α-hydrogen atoms of the trifluoroethoxy groups induced cross-linking that insolubilized 80% of the polymer. The trifluoroethoxy group may retard chain cleavage by a steric shielding of the nearby nitrogen atoms.

From a practical point of view, it appears that the introduction of more than about 10% phenyl substituents by the reaction of phenyllithium with $(NPCl_2)_n$ reduces the molecular weight to an unacceptably low value (<50 000). However, even 10% of a cosubstituent group can have a marked effect on chain packing efficiency or conformational mobility. Hence, such macromolecules should show differences from the alkoxy- or amino-substituted homopolymers. This prospect is discussed later.

Structure of the Polymers. All the high polymers that contained phenyl and trifluoroethoxy or butylamino substituent groups, synthesized by the method shown in Scheme I, were soluble in organic media. Hence, they did not possess a cross-linked structure. The general structure is believed to be derived directly from that of poly(dichlorophosphazene)[14,15] and to be analogous to the structures of the alkoxy-, aryloxy-, or amino-substituted homopolymers.[2-4] This general structure was confirmed by the similarities between the infrared spectra of the polymers produced in this study and those of $[NP(OCH_2CF_3)_2]_n$ and $[NP(NHC_4H_9)_2]_n$, together with the presence of characteristic infrared bands for phenyl groups at 1440 (P–Ph), 3020 (C–H), and 1580, 737, 712, and 688 (aryl) cm^{-1}.

However, a critical question is the disposition of the phenyl groups along the chain. In theory, they could be visualized as being disposed geminally (two phenyl groups per phosphorus), nongeminally (no more than one phenyl group on each phosphorus), or restricted to the chain ends.

The ^{31}P and ^1H NMR data provided tentative evidence that the phenyl groups were arrayed geminally. The polymers of structure VI showed two ^{31}P peaks at 3.65 and 10.7 ppm. Moreover, the peak areas varied according to the degree of phenylation. For example, for the following degrees of phenylation, the ratios of these two peaks are given in parentheses: 8% (11.2:1); 13% (6.8:1); 23% (3.4:1), and 33% (1.9:1). The peak at 3.65 ppm was assigned to the $P(NHC_4H_9)_2$ unit because of the identical chemical shift shown by the homopolymer $[NP(NHC_4H_9)_2]_n$.[3] The 10.07-ppm peak could, therefore, be attributed to either a PPh_2 or a $P(Ph)NHC_4H_9$ structure. However, the ^1H NMR spectra showed phenyl and NHC_4H_9 proton peaks in the same area ratios as the two ^{31}P peaks mentioned above, and this provides marginal evidence that the ^{31}P NMR peak at 10.07 ppm can be attributed to the PPh_2 structure. Geminal phenylation occurs with cyclic oligomeric chlorophosphazenes.[8-10]

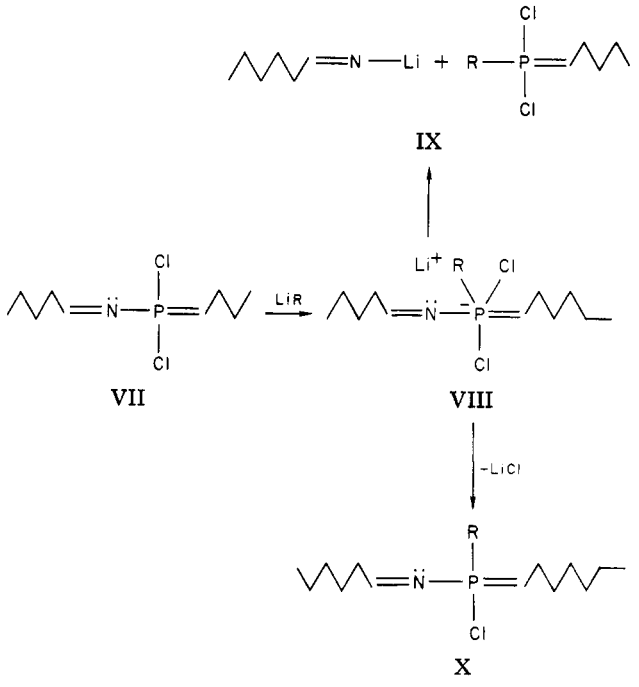
However, the question still remains whether the phenyl groups occupy sites at the chain ends, i.e., at points adjacent to the sites of chain cleavage. First, a comparison of the phenyl content of a number of polymers with their (GPC) average molecular weights led to the conclusion that the number of phenyl groups was, on the average, higher than could be accounted for by the presence of two (or three) phenyl groups at one end of each chain. For example, a polymer of average molecular weight, 1.5×10^5, had an average of 37 phenyl groups per 617 repeating unit chain. Even when the chain length had declined to 200 repeating units, an average of 20 phenyl groups were attached to each molecule. Moreover, the change in glass transition temperatures as the phenyl content of each polymer increased could not be accounted for entirely by the shorter chain length (Table I).

Properties of the Polymers. In appearance, polymers of structures V and VI resemble the homopolymers $[NP(OCH_2CF_3)_2]_n$ or $[NP(NHC_4H_9)_2]_n$. Products of type V are colorless, transparent, or opalescent, film-forming, flexible materials that show a tendency toward low strength only when the molecular weight falls below ≃50 000. The polymers of structure VI are glasses at room temperature. The solubilities also resembled those of the homopolymers. For example, V dissolved in tetrahydrofuran, trifluoroethanol, or piperidine. They were insoluble in aqueous media.

An increase in the number of phenyl groups resulted in an increase in the glass transition temperature. For example, for polymers of structure V, an increase in the phenyl side group percentage in the sequence 0, 5, 9, 15% resulted in an increase in the T_g from −66 to −58, −42, and −30 °C, respectively. This sequence also represents a decrease in average molecular weight from 3×10^6 to 1.5×10^5, 5×10^4, and 3×10^4, and it is not yet possible to predict the molecular weight for polyphosphazenes below which the physical properties become dependent on chain length. However, it seems reasonable to assume that the T_g changes in the molecular weight range above 1×10^5 are a consequence of the different ratios of phenyl to trifluoroethoxy groups. Indeed, a high polymer with 60% phenyl groups and 40% trifluoroethoxy groups, prepared by another synthetic route,[12] had a T_g value of +60 °C. The glass transition temperature is believed to provide a measure of the torsional mobility of the backbone bonds and, hence, these changes can be ascribed to the effect by phenyl groups in sterically restricting the torsional motions of the skeletal bonds. It has already been shown that trifluoroethoxy groups, because of their inherent conformational mobility, permit an unusual degree of skeletal torsional flexibility in $[NP(OCH_2CF_3)_2]_n$.[16,17] Aryl groups bound directly to phosphorus would be expected to raise the barriers to backbone motions and to restrict those motions to minor perturbations from very specific conformations. In fact, it is almost impossible to construct space-filling models of $(NPPh_2)_n$ because of the steric hindrance.

Reaction Mechanism. It is generally assumed that the nucleophilic replacement of chlorine in chlorophosphazenes takes place via the formation of a pentacoordinate tran-

sition state at phosphorus.[18] With substitutions that involve organometallic reagents, a serious mechanistic complication can be envisaged in which the metal of the organometallic species becomes coordinatively bound to the lone pair electrons of a skeletal nitrogen atom (VIII).



Thus, either halogen replacement (X) or chain cleavage (IX) are possible. Which one of these processes predominates will depend on the electron-withdrawing capabilities of those side groups that are already present. If the side group already present is sufficiently electron withdrawing that a significant decrease occurs in the electron density in the lone pair at nitrogen, then metallation may be unimportant, and halogen replacement (X) will predominate. On the other hand, if the electron-withdrawing power of the side group is insufficient to reduce the electron density on nitrogen, then cleavage of the chain will be the principal reaction.

Poly(dichlorophosphazene) appears to lie on the borderline between these two extremes. Although chlorine is an electronegative element, it is not sufficiently electron withdrawing to prevent metal coordination and cleavage. Thus, both substitution and cleavage occur. However, in these terms, it is curious that the phenylation process appears to proceed by a geminal pathway. A phenyl group already attached to phosphorus, being less electronegative than chlorine, would be expected to favor chain cleavage rather than geminal substitution. It is possible that the presence of one phenyl group at phosphorus sterically shields the nearby nitrogen atoms to retard metallation. Alternatively, the high polarizability[19] of the Ph–P–Cl grouping may assist the separation of Cl^- (i.e., cause "metallation" to take place at chlorine rather than at nitrogen).

Chlorine is clearly not sufficiently electronegative to allow the synthesis of highly phenylated high polymers by this route. On the other hand, fluorine is more electronegative than chlorine and, hence, poly(difluorophosphazene) provides a reaction substrate that is less susceptible to skeletal cleavage. This prospect will be discussed in a future paper.

Experimental Section

Materials. Diethyl ether (Fisher, Anhydrous Reagent), *N,N,N′,N′*-tetramethylethylenediamine (TMED) (Eastman), ethylene glycol dimethyl ether (glyme) (Aldrich, Reagent Grade), and tetrahydrofuran (Fisher, Reagent Grade) were dried by distillation from calcium hydride. Toluene (Fisher, Reagent Grade) was dried by azeotropic distillation. Bromobenzene (Fisher, Reagent Grade) was filtered from P_2O_5 and distilled. *n*-Butylamine and triethylamine (Fisher) were dried over potassium hydroxide and distilled immediately before use. Trifluoroethanol (Halocarbon Products, Reagent Grade) was filtered from magnesium sulfate and was stored over molecular sieves. A lithium dispersion in mineral oil (Ventron) was washed with diethyl ether. Dimethylamine (Matheson, anhydrous) and monomethylamine (Matheson, anhydrous) were used without further purification.

Poly(dichlorophosphazene) was prepared by the polymerization of $(NPCl_2)_3$ (kindly supplied by The Firestone Tire and Rubber Co.) at 250 °C.[13] An average of 20–30% conversion to polymer was obtained. Sodium trifluoroethoxide was obtained by the reaction of sodium with trifluoroethanol in THF solution.[4] Phenyllithium in diethyl ether was prepared in the usual manner from bromobenzene and a lithium dispersion.[20] The solution was filtered and standardized by acid–base titration. All manipulations of poly(dichlorophosphazene) and phenyllithium were performed under a nitrogen atmosphere by the use of a glove bag or Schlenk glassware.

Analytical Equipment. Infrared spectra were recorded on a Perkin-Elmer 267 grating spectrometer. ^{31}P, ^{13}C, and ^1H NMR spectra were recorded on a JEOL PS-100 FT NMR spectrometer. Gel permeation chromatography was carried out on Waters Associates instruments (ALC/GPC 50) with 10^5 and 10^6 styragel columns and (Model-6000A unit) with 500, 10^3, 10^4, 10^5, and 10^6 styragel columns for THF solutions. Intrinsic viscosity measurements were made with a Canon Ubbelohde 75-E-157 dilution viscometer, held in a constant temperature water bath at 30 °C. The glass transition temperatures (T_g) were measured with the use of a Chemical Instruments Corp. torsional braid analyzer kindly provided by N.A.S.A., Langley Field. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Synthesis of Phenyl(trifluoroethoxy)phosphazene Polymers. The following procedure is typical: Phenyllithium was prepared from lithium (0.45 g, 0.65 mol) and bromobenzene (3.05 mL, 0.029 mol) in ether solution. The freshly prepared solution of phenyllithium was added dropwise to a solution of poly(dichlorophosphazene) (11.3 g, 0.097 unit mole) in toluene at −20 °C. The reaction mixture was stirred at −20 °C for 1 h. Trifluoroethanol (5 mL, 0.069 mol) was then added to quench the unreacted phenyllithium reagent. Sodium trifluoroethoxide, prepared from sodium (20 g, 0.87 mol) and trifluoroethanol (56.45 mL, 0.78 mol) in tetrahydrofuran (300 mL), was added over 15 min to the reaction mixture. The reaction mixture was then boiled at reflux overnight. Dilute hydrochloric acid was then added to precipitate the product. Further purification was carried out by precipitation from THF into water twice and from THF into benzene twice. The polymer was soluble in THF and acetone. The infrared spectrum showed characteristic absorption bands for trifluoroethoxy and phenylphosphazene groups as follows (in cm^{-1}): 3020 w (C–H); 1420 (P–O–C); 1280 s (P–N); 965, 880 (P–O–C); 750 vw (P–N); 737 w, 712 w, and 688 w (aryl). A ^1H NMR spectrum (in d^6 acetone) showed the unresolved peaks at 4.32 ppm for the trifluoroethoxide group and at 7.42 ppm for the phenyl group. The microanalysis was compatible with the presence of 5% phenyl side groups.

The preparation of the 15% phenyl-substituted product was carried out with the use of the same procedure as described above. The mole ratio of $NPCl_2$ units to phenyllithium was 1:0.7. This reaction was also performed in toluene/diethyl ether solutions. The molecular weights of these polymers were estimated by gel permeation chromatographic analysis in THF. The results are listed in Table I.

Synthesis of Phenyl(*n*-butylamino)phosphazene Polymers. The following procedure is typical of the method used. A freshly prepared solution of phenyllithium (0.028 mol) in diethyl ether was added dropwise to a stirred solution of poly(dichlorophosphazene) (8.2 g, 0.071 unit mol) in toluene at −20 °C. The reaction mixture was stirred at −20 °C for 1 h. Triethylamine (29.8 mL, 0.21 mol) and *n*-butylamine (28 mL, 0.28 mol) were added. The reaction mixture was then stirred for another 24 h.

The product was obtained by precipitation of the concentrated reaction mixture into water. It was then reprecipitated from trifluoroethanol into acetone to remove oligomers. Salts were removed by centrifugation of the polymer solution in THF and by precipitation into water twice. The polymer was dried under vacuum for several days. The solubility properties were similar to those of poly[bis(*n*-butylamino)phosphazene], i.e., the polymer was soluble in trifluoroethanol and chloroform. It was also soluble in THF, whereas the homopolymer is not. The infrared spectrum showed absorption bands similar to those of poly[bis(*n*-butylamino)phosphazene], i.e., at 1250 s (P–N), 910 w (P–N, C–N), and 1190 s (C–N), in addition to the characteristic absorption bands of phenyl groups at 1440 m (P–Ph), 3020 w (C–H), and 1580 w, 737 s, 712 m, 688 m (aryl) cm^{-1}. ^{31}P NMR spectra (in $CDCl_3$) showed two broad singlets at 10.52 and 3.54 ppm relative to H_3PO_4. ^{13}C NMR spectra (in $CDCl_3$) showed peaks at 13.93, 20.36, 34.02, and 41.04 (NHC_4H_9), and a broad singlet at 127.5 ppm (C_6H_5). ^1H NMR spectra (in $CDCl_3$) showed peaks at 0.84, 1.33, 2.78, and 3.88 (NHC_4H_9), and a broad peak at 8.33 ppm (phenyl). The percentage of phenyl substituents on the polymer, as suggested by both ^1H and ^{31}P NMR spectra, was about 8%.

Other reactions were carried out with the same procedure described above. The reactant mole ratios of $NPCl_2$ units to phenyllithium for the generation of the different phenyl contents were: 1:1 (13%), 1:1.5 (23%), and 1:2 (33%). Considerable difficulty was encountered with the reproducibility of the microanalyses of these products. Aminophosphazenes in general suffer from this problem.

Reactions of $(NPCl_2)_n$ with Large Quantities of Phenyllithium. The procedures for these reactions were the same as described above, except that this set of reactions was performed by the addition of a solution of $(NPCl_2)_n$ to a phenyllithium solution. Thus, an excess of phenyllithium was always present.

A solution of poly(dichlorophosphazene) (9.1 g, 0.078 unit mol) in glyme was added to a freshly prepared solution of phenyllithium (0.157 mol) in diethyl ether. Following treatment with sodium trifluoroethoxide and trifluoroethanol, and purification as described above, a ^1H NMR spectrum (d^6 acetone) showed peaks at 4.30 and 7.45 ppm with an area ratio of 3.5:1. ^{31}P NMR spectra showed peaks at −8.48 and 3.33 ppm. (The peak at 3.33 ppm was too broad to integrate.) Microanalysis showed the presence of 9% of phenyl substituent groups. The results are listed in Table I.

The following variations to the reaction conditions were explored.

(a) Effect of Temperature Variations. Reactions were performed at −50, −20, and 0 °C in glyme solution for 1 h (including the addition time of 5 min). The product obtained from the reaction at −50 °C was identical with the product obtained at −20 °C, i.e., with a low percentage of phenyl substituents (~10%) and a high molecular weight (mol wt ~ 10^5). The product obtained from the 0 °C reaction was a low molecular weight product (mol wt < 10^4).

(b) Variation of Reaction Time. Reactions were carried out at −20 °C in glyme solution for 5 min, 1 h, and 5 h. The product obtained from the 5-min reaction was identified as $[NP(NHC_4H_9)_2]_n$. The product obtained after 5 h showed a high percentage of phenyl substituents (30%), but it had a low molecular weight (mol wt < 10^4). ^{13}C NMR spectra gave phenyl resonances at 127.9, 128.6, and 130.9 ppm.

(c) Effect of Reaction Media. Reactions were performed at −20 °C for 1 h in glyme/diethyl ether and toluene/diethyl ether. The ratio of phenylation to chain cleavage was unaffected by this change. This also ruled out the possibility that the process was affected by a reaction of phenyllithium with the etheric solvent[21] since such reactions would be slower in hydrocarbon–ether mixtures.

Reaction of Phenyllithium with a (Trifluoroethoxy)-chlorophosphazene Polymer. A freshly prepared solution of sodium trifluoroethoxide (0.057 mol) in THF was added to a solution of $(NPCl_2)_n$ (6.6 g, 0.057 mol) in toluene. The reaction mixture was boiled at reflux overnight. An ethereal solution of phenyllithium (0.046 mol) was added dropwise to the reaction mixture at 25 °C. The mixture was allowed to stir for 2 h. A freshly prepared solution of sodium trifluoroethoxide in THF was added, and the mixture was stirred overnight. The isolation and purification were identical with those used for phenyl(trifluoroethoxy)phosphazenes. GPC measurements showed a molecular weight of 1.0×10^5. Anal. Calcd for $NP(C_6H_5)_{0.4}(OCH_2CF_3)_{1.6}$: C, 28.72; H, 2.22; N, 5.82; P, 13.23; F, 38.93. Found: C, 28.06; H, 2.90; N, 5.80; P, 13.42; F, 32.49.

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References and Notes

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