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Side-Group Construction in High Polymeric Phosphazenes via Lithiophenoxy Intermediates

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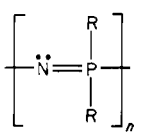
ABSTRACT: The new (lithiophenoxy)phosphazene high polymers $[NP(OC_6H_4Li\text{-}p)_x(OC_6H_4Br)_y]_n$ and $[NP(OC_6H_4Li\text{-}p)_x(OPh)_y]_n$ have been prepared by a metal–halogen exchange reaction between *n*-butyllithium and $[NP(OC_6H_4Br\text{-}p)_2]_n$ or $[NP(OC_6H_4Br\text{-}p)_x(OPh)_y]_n$ at −40 to −60 °C. The lithio derivatives were used as reactive intermediates for the synthesis of polymers of formula $[NP(OC_6H_4X\text{-}p)_x(OC_6H_4Br\text{-}p)_y]_n$, where X = PPh_2 or $PPh_2C_4H_9{}^+Br^-$, or $[NP(OC_6H_4X\text{-}p)_x(OPh)_y]_n$, where X = PPh_2, $PPh_2C_4H_9{}^+Br^-$, $SnPh_3$, $AuPPh_3$, or COOH. Evidence was obtained that the replacement of bromine by lithium is rapid up to the point at which half of the phenoxy groups bear a lithium substituent. Beyond that stage lithiation is extremely slow. The replacement of lithium by the electrophiles $ClPPh_2$, $ClSnPh_3$, $ClAuPPh_3$, or CO_2 was rapid and complete. Quaternization of pendent PPh_2 groups by *n*-butyl bromide was also a facile reaction. The differences between these high polymeric reactions and those of analogous small-molecule cyclic phosphazene model systems are discussed. Comparisons are also made with the lithiation reactions of poly(*p*-bromostyrene).

The synthesis of macromolecules that can function as carrier molecules for catalysts or chemotherapeutic agents or which can selectively bind ions in aqueous media is a subject of growing importance. So also is the preparation of polymers that may serve as templates and supports for the construction of one-dimensional, electrically conducting arrays of metal atoms. We describe here an initial approach to possible solutions of these problems. This approach makes use of the polyphosphazene chain I as a carrier species.



I

The synthesis of a wide range of poly(organophosphazenes) by the interaction of the high polymeric reactive intermediates $(NPCl_2)_n$ (II) or $(NPF_2)_n$ with nucleophiles has been discussed in earlier papers.[1-4] In this paper we describe a new method for the attachment of organic or inorganic residues to polyphosphazene molecules. This synthetic pathway involves a two-step process with the initial attachment of an organic "spacer" side group to the inorganic skeleton, followed by subsequent construction reactions carried out on the organic unit. This route was developed for the following two reasons. First, it was necessary to exclude from consideration any synthetic pathway that involved the reaction of a difunctional reagent with $(NPCl_2)_n$ or $(NPF_2)_n$ because of the inevitable cross-linking that would ensue. The route developed in this work avoids this complication. Second, advantages can be foreseen for the attachment of phosphines, alcohol functions, or carboxylic acid groups to the outer fringes of the side-group structure. Such reactive functionalities could be employed to bind transition metals or could serve as sites for further chemical modification without interference from the polymer skeleton or from the side-group spacer units.

The reaction sequence employed in this work is shown in Scheme I. Exploratory model reactions to test the feasibility of this approach have been carried out with the cyclic phosphazene $(NPCl_2)_3$.[5] In this paper we discuss the reactions shown in Scheme I, together with the unexpected anomalies not encountered with the small-molecule model system. The use of polymer III and its related derivative VII as substrates for lithiation reactions can be compared with the analogous reactions of poly(*p*-bromostyrene).

Results and Discussion

General Reaction Sequence. The reaction sequences shown in Scheme I involve three hitherto unexplored steps: (1) the preparation of high molecular weight polyphosphazenes with the formulas $[NP(OC_6H_4Br\text{-}p)_2]_n$ (III) or $[NP(OC_6H_4Br\text{-}p)_x(OC_6H_5)_y]_n$ (VII); (2) replacement of the bromine atoms in III or VII by lithium with the use of a metal–halogen exchange reaction with *n*-butyllithium; (3) the reaction of (lithiophenoxy)phosphazenes of type IV or VIII with electrophiles such as diphenylchlorophosphine, triphenyltin chloride, (triphenylphosphine)-gold(I) chloride, or carbon dioxide to yield substituted derivatives such as V and IX–XII. These three aspects are discussed in turn.

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Scheme I

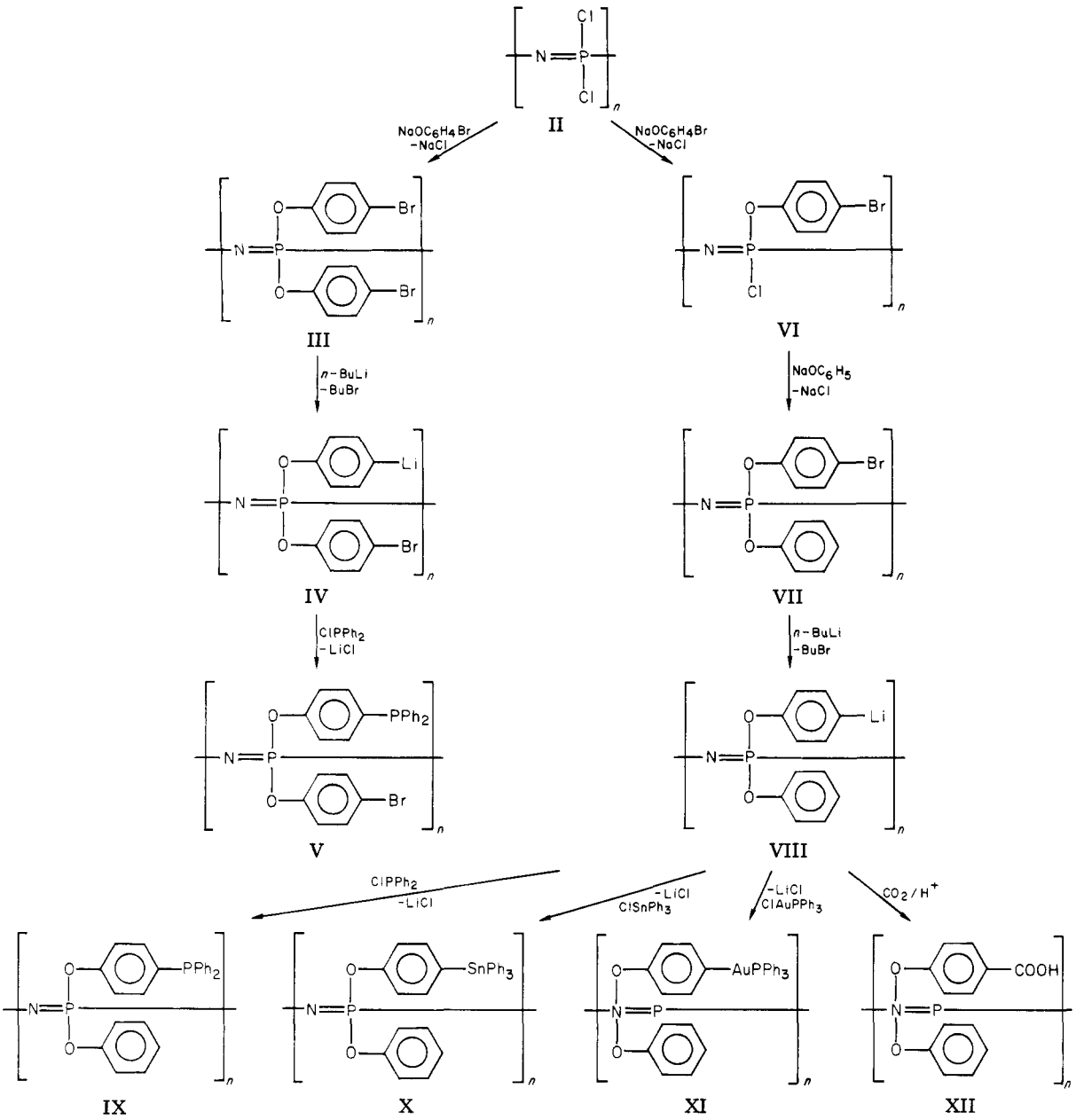


Table I
Properties of
Poly[(*p*-bromophenoxy)phosphazenes]

product[a]	GPC MW[b]	T_g, °C
$[NP(OC_6H_4Br\text{-}p)_2]_n$, III	5×10^5	+44
$[NP(OC_6H_4Br\text{-}p)_{1.12}(OC_6H_5)_{0.88}]_n$, VII (56%)	5×10^5	+21
$[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$, VII (35%)	5×10^5	+8
$[NP(OC_6H_4Br\text{-}p)_{0.4}(OC_6H_5)_{1.6}]_n$, VII (20%)	5×10^5	
$[NP(OC_6H_4Br\text{-}p)_{0.1}(OC_6H_5)_{1.9}]_n$, VII (5%)	5×10^5	+15
$[NP(OC_6H_5)_2]_n$	5×10^5	+14

[a] For the series of polymers represented by VII, the percentages of bromophenoxy residues are given in parentheses. [b] GPC molecular weights are relative to polystyrene standards. [c] Glass transition measurements were obtained with the use of a torsional braid analyzer.

Synthesis, Structure, and Properties of (*p*-Bromophenoxy)-Substituted Polyphosphazenes. Polymers of type III were prepared by the interaction of poly(dichlorophosphazene) (II) with sodium *p*-bromophenoxide. Mixed-substituent species, containing both *p*-bromophenoxy and phenoxy groups, were synthesized by the initial interaction of II with a stoichiometric deficiency of sodium *p*-bromophenoxide, followed by treatment with an excess of sodium phenoxide. Four different polymers corresponding to species of type VII were prepared. In these, the ratio of *p*-bromophenoxy to phenoxy groups was 0.1:1.9, 0.4:1.6, 0.7:1.3, and 1.12:0.88.

Evidence exists that the interaction of aryl oxide ion with II results in a nongeminal substitution pathway.[4,6] Hence, the idealized nongeminal structure depicted in VII probably has some validity. The molecular weights and T_g values for these polymers are listed in Table I. Comparisons of these polymers with samples of $[NP(OC_6H_5)_2]_n$, prepared under identical reaction conditions, showed that the *p*-bromophenoxy substituent group had little effect on the average molecular weight or the glass transition temperature. This is perhaps not surprising because the *p*-bromo functionality can exert very little additional steric

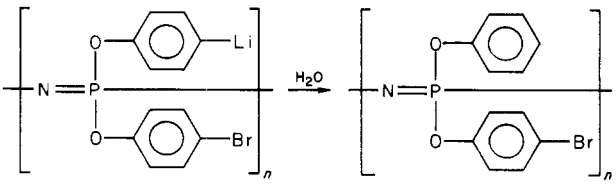
Table II
Polymers Derived from Metal-Halogen Exchange Reactions Followed by Treatment of the Lithiated Derivatives with Water

compn of starting polym	% bromophenoxy substituents after lithiation and reacn with water, lithiation reacn times, h		
	0.5	2	6
$[NP(OC_6H_4Br\text{-}p)_{0.1}(OC_6H_5)_{1.9}]_n$	0		
$[NP(OC_6H_4Br\text{-}p)_{0.4}(OC_6H_5)_{1.6}]_n$	0		
$[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$	2.44		2.14
$[NP(OC_6H_4Br\text{-}p)_{1.12}(OC_6H_5)_{0.88}]_n$	9.29		3.74
$[NP(OC_6H_4Br\text{-}p)_2]_3$	49.1	45.3	30.9

hindrance either during substitution or during chain torsional motion. However, the solubilities of the polymers were changed by the presence of the bromine atoms. When 0, 5, 20, or 35% of the side groups were *p*-bromophenoxy groups, the polymers were soluble in tetrahydrofuran (THF) (warming of the THF was often necessary to accomplish solubilization of the polymers), but polymers with 56 or 100% *p*-bromophenoxy groups were insoluble in THF unless they had been dissolved previously in boiling dioxane. It is conceivable that the *p*-bromophenoxy groups can generate a high degree of microcrystallinity which influences the solubility behavior.

Metal-Halogen Reactions. The metal-halogen exchange reactions[7] were examined for the interaction at −40 to −60 °C in tetrahydrofuran of *n*-butyllithium with species of type VII or III that contained 5, 20, 35, 56, or 100% of the side groups as *p*-bromophenoxy units. The following features were found.

First, the possibility of side reactions during the lithiation process was monitored by treatment of the lithiophosphazene with water to yield products such as XIII. The composition of the products was then established by elemental microanalysis, ^{31}P NMR spectroscopy, and gel permeation chromatography (GPC) molecular weight determinations. The use of these techniques showed that neither chain-scission reactions nor displacement of aryl oxide side groups occurred to a detectable degree at −40 to −60 °C.



IV XIII

Second, by the use of elemental microanalysis, it was found that, although the complete lithiation reaction of the cyclic trimer $[NP(OC_6H_4Br\text{-}p)_2]_3$ is rapid at −40 to −60 °C, the reaction of the polymeric analogue (III) is slower and proceeds in two stages. For example, the metal-halogen exchange process was rapid and nearly complete within 0.5 h for polymers of type VII in which 5, 20, or 35% of the side groups were bromophenoxy units. However, only partial lithiation took place in the same time period when the polymers contained 56 or 100% bromophenoxy groups. In fact, with these latter two polymers the metal-halogen exchange was rapid *up to the point at which 50% of the total number of side groups bore a lithium atom.* Beyond that point, the lithiation reaction was markedly retarded. As shown in Figure 1 and Table II, which illustrate the effect of increasing reaction time on the lithiation of III (followed by treatment with water to yield XIII and subsequent elemental microanalyses), lithiation was rapid in the first 0.5 h, during which time 51% of the bromine atoms had been replaced. Thereafter, the rate of lithiation was so slow that only 18% of the remaining bromine atoms were replaced in the next 5.5 h. The same behavior was shown by a polymer which initially contained 56% *p*-bromophenoxy groups. It appears likely that the presence of one lithiophenoxy unit inhibits the introduction of a second lithium atom at an aryloxy unit geminal to the first, perhaps by charge repulsion or possibly by aggregation of the aryllithium units. Evidence in favor of this interpretation was provided by the following experiment. Polymer III was allowed to undergo a prolonged reaction with *n*-butyllithium until 70% of the *p*-bromophenoxy groups had been converted to *p*-lithiophenoxy groups. Reaction of this compound with water yielded a product similar to XIII. Subsequent lithiation of this product was rapid and virtually complete. Hence, removal of the bound lithium component apparently removed the inhibiting factor.

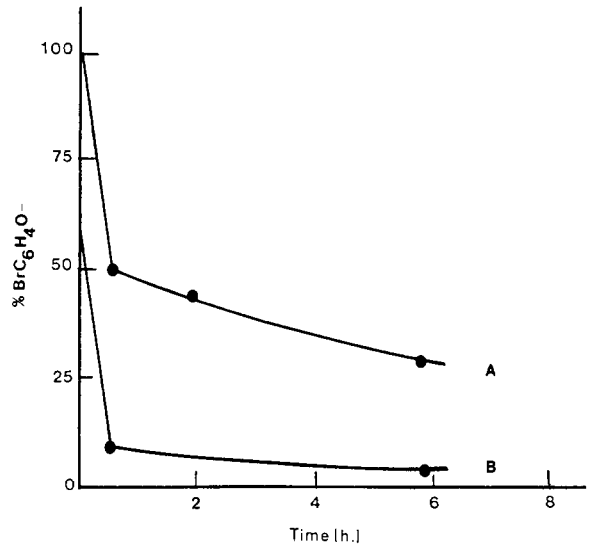


Figure 1. Plot of the percent remaining *p*-bromophenoxy pendent groups vs. reaction time following the reaction with excess *n*-butyllithium for polymers that possessed initially 100% *p*-bromophenoxy substituent groups (polymer III, curve A) and 56% *p*-bromophenoxy, 44% phenoxy substituent groups (polymer VII, curve B). The percentages of residual *p*-bromophenoxy groups were obtained by elemental microanalytical determinations for bromine after deactivation of the lithiated derivatives with water and conversion of lithioaryl groups to aryl. The curves illustrate the dramatic decrease in lithiation rate after approximately 50% of the pendent groups have reacted.

A similar deactivation effect occurred during the metal-halogen exchange reaction between *n*-butyllithium and poly(*p*-bromostyrene). At −50 °C in THF solvent, only 84% of the bromine atoms were replaced by lithium during 6 h.[8] Presumably the effect is less marked than with III because only one aryl group is attached to each skeletal linkage atom.

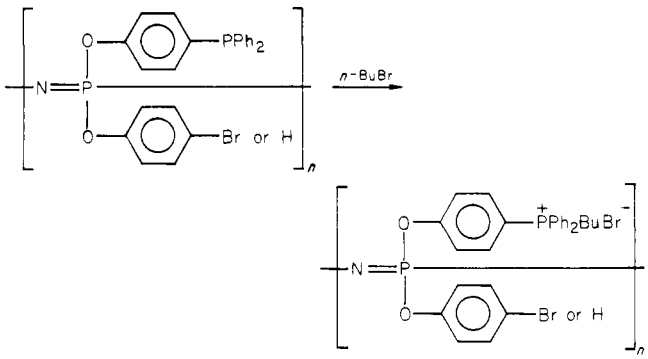
Cross-Linking at 25 °C. The reactions discussed in this paper require that the lithiation of III or VII and the subsequent reactions of IV or VIII must take place at low temperatures (−40 to −60 °C). At higher temperatures, cross-linking reactions take place. For example, if polymers of type VII (35% *p*-bromophenoxy, 65% phenoxy groups) were treated with *n*-butyllithium at −40 and −60 °C and the reaction mixture was treated with water at the same temperature, un-cross-linked species of type XIII were formed. However, if the reaction mixture was allowed to warm to 25 °C before treatment with water, the product was cross-linked and insoluble. It was shown that this

cross-linking reaction was associated with the presence of aryl–lithium bonds, because treatment of the polymer $[NP(OC_6H_5)_2]_n$ with *n*-butyllithium at −50 °C, followed by warming to 25 °C and addition of water, did not yield a cross-linked polymer.

(Lithiophenoxy)phosphazene polymers could cross-link by a number of different mechanisms. First, intermolecular aryl coupling reactions could take place between *p*-lithiophenoxy and *p*-bromophenoxy substituent groups to form *p*-biphenylenedioxy cross-links. Second, benzyne formation from *p*-bromophenoxy groups is possible, followed by coupling to *p*-lithiophenoxy residues. Third, a lithioaryl unit could attack a phosphorus with displacement of a *p*-bromophenoxy residue and formation of a P–O–C_6H_4–P linkage. We favor this third mechanism. It has been reported previously[9] that the phenoxide groups can be displaced from the cyclic trimer $[NP(OC_6H_5)_2]_3$ by organolithium reagents at normal temperatures. Moreover, it was shown here that the treatment of $[NP(OC_6H_5)_2]_3$ with phenyllithium yielded a mixture of products which contained the compound $[N_3P_3(C_6H_5)(OC_6H_5)_5]$ (see Experimental Section).

Interaction of Poly[(lithiophenoxy)phosphazenes] with Diphenylchlorophosphine. Polymers of type VII or III with 5, 20, 35, 56, or 100% of the side groups as *p*-bromophenoxy units were subjected to lithium–halogen exchange reactions as described in the preceding sections. Treatment of the lithiophenoxy derivatives at −40 to −60 °C with diphenylchlorophosphine resulted in a high-yield attachment of diphenylphosphorus residues to the phenoxy units to give products such as V or IX. The reaction conditions are summarized later. The coupling reactions with diphenylchlorophosphine appeared to be as efficient as those with water. The triarylphosphine unit is a valuable ligand for coordination to transition-metal catalyst systems,[10-12] and this aspect will be discussed in a later paper.

The synthesis of V and IX was complicated by the concurrent formation of low percentages of butylphosphonium salts XIV. The degree of phosphonium salt



XIV

formation in the conventional synthesis is listed in Table III. Presumably the quaternization reaction is a consequence of the liberation of *n*-butyl bromide during the metal–halogen exchange process. The phosphonium salts were detected by three techniques. ^1H NMR spectroscopy was used to demonstrate the presence of butyl groups in the purified polymer. ^{31}P NMR spectra of a polymer type IX, in which 35% of the aryloxy groups bore phosphorus-containing pendent groups, possessed a resonance at +24 ppm which was compatible with the presence of a phosphonium salt unit. This corresponded to approximately 3.1% of all the phosphine groups present (the backbone ^{31}P resonance was at −20 ppm and the phosphine resonance was at −8 ppm).[13] Moreover, partial proton-decoupling experiments revealed that the resonance at +24 ppm was coupled to both aryl and alkyl protons. Finally, it was shown that the addition of an excess of butyl bromide to the polymer brought about a complete disappearance of the −8 ppm resonance and a concurrent growth in the size of the peak at +24 ppm. Polymeric butylphosphonium salts are possible precursors for polymer-supported reactions[14] or for use as phase-transfer catalysts.[15]

It is not obvious why the analogous cyclic model compound $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_2]_3$ was less prone to phosphonium salt formation during its synthesis. However, conversion of 50% of the phosphine groups to phosphonium units could be effected in the trimeric system by treatment with an excess of butyl bromide during 48 h at 80 °C.

Interaction of (Lithiophenoxy)phosphazenes with Triphenyltin Chloride, (Triphenylphosphine)gold(I) Chloride, or Carbon Dioxide. As shown in Scheme I, lithio derivatives of type VIII were used for the attachment of triphenyltin, (triphenylphosphine)gold(I), or carboxylic acid functions to the (aryloxy)phosphazene structure, with the formation of X, XI, or XII. Specifically, polymers of formula $[NP(OC_6H_4SnPh_3\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$, $[NP(OC_6H_4AuPPh_3\text{-}p)_{0.52}(OC_6H_5)_{1.48}]_n$, and $[NP(OC_6H_5COOH\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$ were isolated in high yields. The details of the synthetic procedures are summarized in the Experimental Section. The derivative $[NP(OC_6H_4COOH\text{-}p)_{1.42}(OC_6H_4Br\text{-}p)_{0.58}]_n$ was also prepared in high yield from the interactions of IV with carbon dioxide.

Experimental Section

Equipment. ^{31}P NMR spectra were obtained in the Fourier transform mode at 40.4 MHz with a JEOL PS-100 FT spectrometer and processed with a Nicolet 1080 computer. ^1H NMR spectra were obtained with the same spectrometer operated at 100 MHz. Infrared spectra were recorded with a Perkin-Elmer Model PE 580 high-resolution infrared spectrophotometer. Approximate polymer molecular weights were determined with a Waters Associates AIC/GPC 501 instrument fitted with a 120 cm × 1 cm 10^6 Styragel column.[16] Glass transition temperatures (T_g) were measured with a Chemical Instruments Corp. torsional braid analyzer kindly provided by NASA, Langley Field.

Materials. All experimental manipulations were performed under an atmosphere of dry nitrogen (Matheson). Tetrahydrofuran (THF) (Fisher) and dioxane (Fisher) were freshly distilled under nitrogen from sodium benzophenone ketyl. Poly(dichlorophosphazene), $(NPCl_2)_n$, was prepared by the melt polymerization of $(NPCl_2)_3$ (Ethyl Corp.) by methods described previously.[17] *n*-Butyllithium was used as received (Foote Mineral; 1.6 M solution in hexane). Phenol, *p*-bromophenol (Aldrich), diphenylchlorophosphine (Orgmet), triphenyltin chloride (Strem), (triphenylphosphine)gold(I) chloride (Strem), and sodium hydride (Alfa) were used as received.

Elemental Microanalyses. The accuracy of elemental microanalyses, as determined by Galbraith Laboratories, was found to be dependent on the element that was analyzed and the composition of the polymeric compounds. Elemental analyses for bromine proved to be the most reliable indicator of polymer compositions. Furthermore, the polymers that possessed exclusively *p*-bromophenoxy substituent groups and those that contained only phenoxy and *p*-bromophenoxy substituent groups yielded the most accurate microanalytical data. The compositions of polymers that possessed phosphine residues could be determined by ^{31}P NMR peak area integrations of the phosphazene and phosphine phosphorus resonances. The ratios of phosphazene to phosphine, as determined by ^{31}P NMR methods, agreed to within 3% of the value determined by elemental microanalyses for bromine.

General Procedure for the Synthesis of Polymers with the Formulas $[NP(OC_6H_4Br\text{-}p)_2]_n$ (III) and $[NP(OC_6H_4Br\text{-}p)_x(OC_6H_5)_y]_n$ (VII). The specific reaction conditions used for

Table III
Polymers Derived from the Metal-Halogen Exchange Reaction and Subsequent Treatment with Diphenylchlorophosphine

	phosphine-substituted product		
starting polym	% OC_6H_4Br	% $OC_6H_4P(C_6H_5)_2$ [a]	% $OC_6H_4P(C_6H_5)_2C_4H_9^+Br^-$ [b]
$[NP(OC_6H_4Br\text{-}p)_{0.1}(OC_6H_5)_{1.9}]_n$	0	5	
$[NP(OC_6H_4Br\text{-}p)_{0.4}(OC_6H_5)_{1.6}]_n$	0	20	
$[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$	2.5	31.3	1.2
$[NP(OC_6H_4Br\text{-}p)_{1.12}(OC_6H_5)_{0.88}]_n$	9.3	40.3	6.2
$[NP(OC_6H_4Br\text{-}p)_2]_n$	49.1	47.3	3.7

[a] The values for pendent phosphine groups are derived from elemental microanalyses for bromine and confirmed by ^{31}P NMR peak area integrations (error in the ^{31}P NMR technique is ±3%). The NMR spectra were obtained for solution of the polymers in THF. [b] The values for butylphosphonium salt formation are derived from elemental microanalyses for bromine and confirmed by ^{31}P NMR peak area integrations.

Table IV
Reaction Conditions for the Preparation of Poly[(*p*-bromophenoxy)phosphazenes]

polym synthesized	$(NPCl_2)_n$, g (mol)	*p*-bromophenol, g (mol)	NaH, g	phenol, g (mol)	NaH, g	% yield
$[NP(OC_6H_4Br\text{-}p)_{0.1}(OC_6H_5)_{1.9}]_n$	3.8 (0.033)	0.57 (0.0033)	5	80 (0.85)	31	>50
$[NP(OC_6H_4Br\text{-}p)_{0.4}(OC_6H_5)_{1.6}]_n$	4.0 (0.035)	2.39 (0.014)	5	27 (0.71)	35	>50
$[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$	4.3 (0.037)	6.41 (0.037)	10	39 (0.42)	22	>50
$[NP(OC_6H_4Br\text{-}p)_{1.12}(OC_6H_5)_{0.88}]_n$	4.0 (0.035)	8.95 (0.053)	10	40 (0.43)	21	>50
$[NP(OC_6H_4Br\text{-}p)_2]_n$	3.0 (0.026)	9.0 (0.52)	25			>50

these syntheses are listed in Table IV. The general experimental procedure was as follows. Sodium *p*-bromophenoxide was prepared by adding a solution of *p*-bromophenol in dioxane (100 mL of dioxane was usually employed) to a stirred suspension of a molar excess of sodium hydride and dioxane (100 mL). After 4 h, the reaction mixture was heated to reflux and filtered. The filtrate was added to a stirred solution of poly(dichlorophosphazene) in dioxane (150 mL). The reaction mixture was stirred for 4–8 h at 25 °C and then added to a solution of sodium phenoxide, prepared in a similar manner to the preparation of sodium *p*-bromophenoxide, in boiling dioxane (250 mL). The reaction mixtures were refluxed for 168 h and concentrated by rotoevaporation, and the concentrate was added to water. The precipitate was collected, washed with ethanol, redissolved in hot tetrahydrofuran [polymer VII (with 56% *p*-bromophenoxy groups) was not soluble in THF and so hot dioxane was used as the solvent for this compound], and precipitated into water. The reprecipitation procedure was carried out once from THF into water, from THF into ethanol, and from THF into pentane. The yields of the polymers represented by VII exceeded 50%. The microanalytical data obtained for these polymers are listed in Table V.

The preparation of polymer III was carried out in the following way. A solution of sodium *p*-bromophenoxide in dioxane, prepared by the method described in the preceding section, was heated to reflux and filtered into a reaction vessel (three-necked, 1-L capacity). A solution of poly(dichlorophosphazene) in dioxane (150 mL) was added dropwise to the sodium *p*-bromophenoxide solution at reflux. The reaction mixture was heated at reflux for 168 h and concentrated by rotoevaporation, and the concentrate was added to water. The precipitate was washed with ethanol and an unsuccessful attempt was made to dissolve the polymer in tetrahydrofuran. The polymer was recovered from tetrahydrofuran by filtration and then dissolved in boiling dioxane. The hot solution was filtered and reprecipitated into water. The recovered polymer was redissolved in boiling dioxane and reprecipitated once again into water. The polymer was further reprecipitated from dioxane into ethanol and then from dioxane into pentane. The yield of III was 30%. The microanalytical results obtained for III are listed in Table V.

Preparation of $[NP(OC_6H_5)_2]_n$.[18] A solution of phenol (33 g, 0.35 mol) in dioxane (100 mL) was added dropwise to a stirred suspension of sodium hydride (17 g, as a dispersion in oil) and dioxane (100 mL). The reaction mixture was boiled at reflux to ensure complete reaction. The hot reaction mixture was filtered and the filtrate was added to a reaction vessel (three-necked, 1-L capacity). To this boiling solution was added dropwise a solution of poly(dichlorophosphazene) (4.0 g, 0.035 mol) in dioxane (200 mL). The reaction mixture was then refluxed for 168 h, concentrated by rotoevaporation, and added to water. The precipitate was collected, washed with ethanol, and redissolved in hot THF, and the polymer was reprecipitated into water once again. Reprecipitations were carried out from THF into water for a third time and from THF into ethanol. The yield of $[NP(OC_6H_5)_2]_n$ was over 50%. The microanalytical data obtained for this polymer are listed in Table V.

General Experimental Procedure for the Preparation of Polymers with *p*-Lithiophenoxy Substituent Groups. Polymers with *p*-lithiophenoxy substituent groups were prepared by reacting III or VII with *n*-butyllithium. Specific experimental details are listed in Table V. A general procedure for the metal–halogen exchange reactions with VII or III is as follows. The polymers VII (with 5, 20, and 35% *p*-bromophenoxy groups) were dissolved in THF (200 mL). Polymers III and VII (56% bromophenoxy groups) required a two-step procedure that involved the use of boiling dioxane, removal of the dioxane by means of a rotary evaporator, and treatment with THF (200 mL). When this procedure was employed, THF-soluble forms of III and VII (56% bromophenoxy) could be obtained. The solutions of III or VII in THF were cooled to −40 to −60 °C by means of a dry ice–acetone bath (before this step, the reaction vessels were fitted with a rubber septum). *n*-Butyllithium (4–6 mL) was then added to the polymer solutions via syringe. This resulted in the immediate formation of yellow or green reaction mixtures. Reaction times with *n*-butyllithium were in the range of 0.5–6 h (the most commonly employed reaction time was 0.5 h). The lithiated derivatives were deactivated by treatment with water, diphenylchlorophosphine, carbon dioxide, triphenyltin chloride, or (triphenylphosphine)gold(I) chloride. These reaction procedures are discussed in the following sections.

General Experimental Procedure for the Deactivation of *p*-Lithiophenoxy Substituent Groups with Water. The lithiated derivatives that were prepared by metal–halogen exchange reactions of *n*-butyllithium with polymers III or VII (5, 20, 35, and 56% *p*-bromophenoxy groups) were characterized after their deactivation with water. The specific experimental details involved in these reaction sequences are listed in Table VI. The deactivations of the lithiated intermediates were carried out by the addition of water (by syringe) to the reaction mixtures at −40 to −60 °C. After the addition of water, the reaction mixtures were allowed to warm to 25 °C. The polymeric products were isolated by filtration and purified by reprecipitations from THF into water, from THF into ethanol, and from THF into pentane. The microanalytical data obtained for the polymers following water deactivation of the lithiated intermediates IV or VIII are listed in Table V.

Table V
Table of Analytical Results

polym structure		% C	% H	% Br
$[NP(OC_6H_5)_2]_n$[a]	calcd	62.34	4.33	
	found	60.15	4.33	
$[NP(OC_6H_4Br)_{0.1}(OC_6H_5)_{1.9}]_n$,[a,b] VII (5%)	calcd	60.47	4.16	3.04
	found	60.38	4.35	3.04
$[NP(OC_6H_4Br)_{0.4}(OC_6H_5)_{1.6}]_n$, VII (20%)	calcd	54.84	3.66	12.18
	found	54.16	4.01	12.16
$[NP(OC_6H_4Br)_{0.7}(OC_6H_5)_{1.3}]_n$,[a] VII (35%)	calcd	50.33	3.25	19.50
	found	51.03	3.71	19.45
$[NP(OC_6H_4Br)_{1.12}(OC_6H_5)_{0.88}]_n$,[a] VII (56%)	calcd	45.09	2.78	28.02
	found	42.40	2.78	28.01
$[NP(OC_6H_4Br)_2]_n$[a,c] III	calcd	37.04	2.06	41.10
	found	37.13	2.08	40.96
$[NP(OC_6H_5)_2]_n$[d]	calcd	62.34	4.33	0.00
	found	56.70	3.99	<0.15
$[NP(OC_6H_5)_2]_n$[e]	calcd	62.34	4.33	0.00
	found	61.38	4.35	<0.15
$[NP(OC_6H_4Br)_{0.05}(OC_6H_5)_{1.95}]_n$[f]	calcd	61.32	4.24	1.66
	found	61.62	4.24	1.66
$[NP(OC_6H_4Br)_{0.19}(OC_6H_5)_{1.81}]_n$[g]	calcd	57.87	3.97	6.04
	found	58.62	3.99	6.04
$[NP(OC_6H_4Br)_{0.98}(OC_6H_5)_{1.02}]_n$[h]	calcd	46.69	2.92	26.42
	found	44.89	2.73	25.33
$[NP(OC_6H_4Br)_{0.9}(OC_6H_5)_{1.1}]_n$[i]	calcd	47.61	3.01	23.92
	found	45.91	3.21	23.91
$[NP(OC_6H_4Br)_{0.04}(OC_6H_5)_{1.96}]_n$[j]	calcd	60.73	4.39	1.46
	found	61.44	4.25	1.46
$[NP(OC_6H_4Br)_{0.07}(OC_6H_5)_{1.93}]_n$[k]	calcd	60.79	4.19	2.52
	found	59.20	3.89	2.52
$[NP(OC_6H_4Br)_{0.62}(OC_6H_5)_{1.38}]_n$[l]	calcd	51.47	3.35	17.65
	found	45.56	2.84	17.61
$[NP(OC_6H_4P(C_6H_5)_2)_{0.1}(OC_6H_5)_{1.9}]_n$[m]	calcd	63.52	4.37	0.00
	found	63.60	4.28	0.17
$[NP(OC_6H_4P(C_6H_5)_2)_{0.4}(OC_6H_5)_{1.6}]_n$[n]	calcd	66.08	4.47	0.19
	found	64.54	4.71	0.19
$[NP(OC_6H_4Br)_{0.05}(OC_6H_5)_{1.3}(OC_6H_4P(C_6H_5)_2)_{0.63}(OC_6H_4P(C_6H_5)_2(C_4H_9)^+Br^-)_{0.024}]_n$[o]	calcd	66.73	4.06	1.62
	found	57.96	4.48	1.61
$[NP(OC_6H_4Br)_{0.19}(OC_6H_5)_{0.58}(OC_6H_4P(C_6H_5)_2)_{0.81}(OC_6H_4P(C_6H_5)_2(C_4H_9)^+Br^-)_{0.12}]_n$[p]	calcd	65.50	4.45	5.66
	found	62.43	4.15	5.67
$[NP(OC_6H_4Br)_{0.98}(OC_6H_9P(C_6H_5)_2)_{0.95}(OC_6H_4P(C_6H_5)_2(C_4H_9)^+Br^-)_{0.07}]_n$[q]	calcd	58.16	3.73	16.64
	found	56.61	3.68	16.65
$[NP(OC_6H_4COOH)_{0.7}(OC_6H_5)_{1.3}]_n$[r]	calcd	58.17	3.83	
	found	57.86	3.77	0.2
$[NP(OC_6H_4COOH)_{1.42}(OC_6H_4Br)_{0.58}]_n$[s]	calcd			13.68
	found			13.86
$[NP(OC_6H_4Sn(C_6H_5)_3)_{0.7}(OC_6H_5)_{1.3}]_n$[t]	calcd	62.14	4.17	
	found	60.12	3.80	0.3

[a] Percentage of chlorine in samples: $[NP(OC_6H_5)_2]_n$, 0.30%; VII (5%), 0.19%; VII (20%), 0.20%; VII (35%), 0.28; VII (56%), 0.27%; III, 0.046%. [b] Calcd: P, 12.73; N, 5.70. Found: P, 13.70; N, 5.88. [c] Calcd: P, 7.97; N, 3.60. Found: P, 7.87; N, 3.46. [d] From lithiation of VII (5%) (0.5 h) and water quench. [e] From lithiation of VII (20%) (0.5 h) and water quench. [f] From lithiation of VII (35%) (0.5 h) and water quench. [g] From lithiation of VII (56%) (0.5 h) and water quench. [h] From lithiation of III (0.5 h) and water quench. [i] From lithiation of III (2 h) and water quench. [j] From lithiation of VII (35%) (6 h) and water quench. [k] From lithiation of VII (56%) (6 h) and water quench. [l] From lithiation of III (6 h) and water quench. [m] From lithiation of VII (5%) (0.5 h) and diphenylchlorophosphine quench. [n] From lithiation of VII (20%) (0.5 h) and diphenylchlorophosphine quench. [o] From lithiation of VII (35%) (0.5 h) and diphenylchlorophosphine quench. [p] From lithiation of VII (56%) (0.5 h) and diphenylchlorophosphine quench. [q] From lithiation of III (0.5 h) and diphenylchlorophosphine quench. [r] From lithiation of VII (35%) (0.5 h) and CO_2 quench and then acid treatment. Oxygen analysis: calcd, 20.78; found, 22.34. [s] From lithiation of III (6 h) and CO_2 quench and then acid treatment. Oxygen analysis: calcd, 22.82; found, 22.76. [t] From lithiation of VII (35%) (0.5 h) and triphenyltin chloride.

General Experimental Procedure for the Reactions of *p*-Lithiophenoxy Substituent Groups with Diphenylchlorophosphine. Metal–halogen exchange reactions were carried out on polymers III or VII (5, 20, 35, and 56% *p*-bromophenoxy groups) and the resultant lithiated intermediates were deactivated with diphenylchlorophosphine (see Table VII for specific details). Diphenylchlorophosphine was added via syringe to the reaction mixture at −40 to −60 °C. The low reaction temperatures were maintained for 3 h, and the reaction mixture was then allowed to warm to 25 °C. Ethanol (100 mL) was added to the reaction mixture which was then concentrated by rotoevaporation until the polymer precipitated from solution. The polymeric precipitate was collected by filtration, washed with ethanol, dissolved in THF, and precipitated into ethanol. Reprecipitation was carried out from THF into ethanol for a second time and then from THF into pentane. Microanalytical data and T_g data obtained for the series of polymers prepared by this general method are listed in Tables V and VII. The ^{31}P NMR spectra of the polymers that possessed pendent phosphine residues consisted of a resonance at −20 ppm (phosphazene phosphorus), a resonance at −8 ppm (phosphine phosphorus), and a small resonance at +22 to +24 (assigned to pendent butylphosphonium bromide residues). These spectra were referenced to an external H_3PO_4 sample and employed a D_2O capillary lock. The integrated peak areas for these polymers were used as a method for the determination of polymer compositions.

Synthesis of $[NP(OC_6H_4Sn(C_6H_5)_3\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$ (X). A sample of $[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$, VII (35% bromophenoxy groups) (0.5 g, 0.0017 mol), was dissolved in THF (350 mL). This solution was then cooled to −60 °C and *n*-butyllithium

Table VI
Reaction Conditions for Water Deactivation of Poly[(p-lithiophenoxy)phosphazenes]

starting polym,[a] g (mol)	n-BuLi, mL (mol)	reacn time, h	water, mL (mol)
VII (5%), 0.50 (0.0021)	4 (0.0064)	0.5	4 (0.22)
VII (20%), 0.50 (0.0019)	4 (0.0064)	0.5	4 (0.22)
VII (35%), 0.58 (0.0020)	4 (0.0064)	0.5	4 (0.22)
VII (35%), 0.58 (0.0020)	4 (0.0064)	6	4 (0.22)
VII (56%), 0.58 (0.0018)	5 (0.008)	0.5	5 (0.28)
VII (56%), 0.54 (0.0017)	5 (0.008)	6	5 (0.28)
III, 0.55 (0.0014)	6 (0.0096)	0.5	6 (0.33)
III, 0.62 (0.0016)	6 (0.0096)	2	6 (0.33)
III, 0.54 (0.0014)	6 (0.0096)	6	6 (0.33)

[a] Percent bromophenoxy substituent groups in parentheses.

Table VII
Conditions for the Reaction of Poly[(p-lithiophenoxy)phosphazenes] with Diphenylchlorophosphine

starting polym,[a] mL (mol)	n-C_4H_9Li, mL (mol)	reacn time, h	ClP-$(C_6H_5)_2$, mL (mol)	product[b]
VII (5%), 0.50 (0.0021)	4 (0.0064)	0.5	4 (0.018)	c
VII (20%), 0.50 (0.0019)	4 (0.0064)	0.5	6 (0.027)	d
VII (35%), 0.57 (0.0020)	4 (0.0064)	0.5	8 (0.036)	e
VII (56%), 0.61 (0.0001)	5 (0.0080)	0.5	10 (0.045)	f
III, 0.62 (0.0016)	6 (0.0096)	0.5	12 (0.054)	g

[a] Percent bromophenoxy substituent groups in parentheses. [b] Product compositions were determined from elemental microanalytical data obtained for bromine. These calculations are based on the assumption that the metal-halogen exchange reaction proceeds to the same point as determined for the proton-quenching experiments (see Table II). ^{31}P NMR data for this phosphine series implied that this assumption is accurate. [c] $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_{0.1}(OC_6H_5)_{1.9}]_n$: $T_g = +8$ °C. [d] $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_{0.4}(OC_6H_5)_{1.6}]_n$. [e] $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_{0.63}(OC_6H_4P(C_6H_5)_2(C_4H_9)(C_4H_9)^+Br^-\text{-}p)_{0.02}(OC_6H_4Br\text{-}p)_{0.05}(OC_6H_5)_{1.3}]_n$: $T_g = +17$ °C. [f] $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_{0.81}(OC_6H_4P(C_4H_9)Br\text{-}p)_{0.12}(OC_6H_4Br\text{-}p)_{0.19}(OC_6H_5)_{0.88}]_n$. [g] $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_{0.95}(OC_6H_4P(C_6H_5)_2Br\text{-}p)_{0.07}(OC_6H_4Br\text{-}p)_{0.98}]_n$: $T_g = +35$ °C.

(5 mL, 0.008 mol) was added. The reaction mixture was stirred for 1 h at −60 °C, and a solution of triphenyltin chloride (6.5 g, 0.017 mol) in THF (75 mL) was added. The reaction mixture was stirred at −60 °C for 3 h, allowed to warm to 25 °C, and stirred for 14 h. The reaction mixture was concentrated by rotoevaporation and reprecipitated into a dilute aqueous HCl solution. The polymeric product was collected by filtration and then reprecipitated from THF into water and from THF into n-pentane. The product showed a low solubility in THF. Microanalytical data were consistent with the formula $[NP(OC_6H_4Sn(C_6H_5)_3\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$ (see Table V).

Synthesis of $[NP(OC_6H_4AuP(C_6H_5)_3\text{-}p)_{0.52}(OC_6H_5)_{1.48}]_n$ (XI). A sample of $[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$, VII (35% bromophenoxy groups) (0.5 g, 0.0017 mol), was dissolved in THF (200 mL). This solution was then cooled to −60 °C and n-butyllithium (0.6 mL, 0.0010 mol) was added. The reaction mixture was stirred for 1 h at −60 °C, and a solution of (triphenylphosphine)gold(I) chloride (0.50 g, 0.0010 mol) in 25 mL of THF was added. The reaction mixture was stirred for 3 h at −60 °C, allowed to warm to 25 °C, and stirred for 1 h. Water (0.5 g, 0.028 mol) was added, the reaction mixture was concentrated by rotoevaporation, and the mixture was filtered. The filtrate was added to n-pentane and the precipitate was collected. A ^{31}P NMR spectrum of the product showed resonances at +33 and −20 ppm, assigned to phosphine and phosphazene phosphorus atoms, respectively. The integrated areas for these resonances were consistent with the formula $[NP(OC_6H_4AuP(C_6H_5)_3\text{-}p)_{0.52}(OC_6H_5)_{1.48}]_n$. Solutions of XI in THF showed signs of decomposition (purple color formation) after only 3 h in air. $C_6H_5AuP(C_6H_5)_3$ and the cyclic phosphazene $[NP(OC_6H_4AuP(C_6H_5)_3\text{-}p)_2]_3$ showed no decomposition in the solid state. (These compounds were only slightly soluble in THF. Hence, their solution stability could not be evaluated.)

Synthesis of $[NP(OC_6H_4COOH\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$ (XII). A sample of $[NP(OC_6H_4Br\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$, VII (35% bromophenoxy groups) (0.5 g, 0.0017 mol), was dissolved in THF (300 mL). This solution was cooled to −60 °C and n-butyllithium (5 mL, 0.008 mol) was added. The reaction mixture was stirred for 1 h at −60 °C and then added to a large excess of dry ice in a nitrogen-filled glovebag. The reaction mixture was allowed to warm to 25 °C (in a nitrogen atmosphere), and the white polymeric product was collected by filtration. This was then stirred in an aqueous solution of HCl for 20 min and was once again collected by filtration. This compound proved to be insoluble in THF, boiling dioxane, ethanol, water (pH 7 or 12), or a THF solution that contained 20 or 50% (by volume) of triethylamine. The infrared spectrum of the polymeric product suggested the presence of carboxylic acid functions (OH stretch at 3300 cm^{-1} and C=O stretch at 1750 cm^{-1}). Microanalysis of this compound was consistent with the formula $[NP(OC_6H_4COOH\text{-}p)_{0.7}(OC_6H_5)_{1.3}]_n$ (see Table V).

In a similar manner, the derivative $[NP(OC_6H_4COOH\text{-}p)_{1.42}(OC_6H_4Br\text{-}p)_{0.58}]_n$ (Table V) was prepared by the interaction of $[NP(OC_6H_4Br\text{-}p)_2]_n$ (III) (0.5 g, 0.0013 mol) with n-butyllithium (4 mL, 0.0064 mol) for 6 h, followed by treatment with carbon dioxide.

Synthesis of $[NP(OC_6H_4Br\text{-}p)_{0.05}(OC_6H_4P(C_6H_5)_2(C_4H_9)^+Br^-\text{-}p)_{0.65}(OC_6H_5)_{1.30}]_n$. A sample of $[NP(OC_6H_4Br\text{-}p)_{0.050}(OC_6H_4P(C_6H_5)_2\text{-}p)_{0.626}(OC_6H_4P(C_6H_5)_2(C_4H_9)^+Br^-\text{-}p)_{0.024}(OC_6H_5)_{1.30}]_n$ (0.5 g, 0.0014 mol), prepared from the reaction of VII (35% bromophenoxy) with n-butyllithium, followed by treatment with diphenylchlorophosphine (see Table VII), was dissolved in THF (200 mL), and an excess of n-butyl bromide (2 g, 0.015 mol) was added. The reaction mixture was stirred for 1 h at 25 °C, and ethanol (300 mL) was added. The reaction mixture was evaporated to dryness in a rotary evaporator. The polymeric product was purified by reprecipitations from THF into water and from THF into ethanol. The polymer showed only two ^{31}P NMR resonances at +24 (phosphonium salt phosphorus) and −20 ppm (phosphazene phosphorus). No resonance at −8 ppm (phosphine phosphorus) could be detected from this sample. ^{31}P NMR peak area integrations were consistent with the polymer structure $[NP(OC_6H_4Br\text{-}p)_{0.50}(OC_6H_4(C_6H_5)_2(C_5H_9)^+Br^-\text{-}p)_{0.65}(OC_6H_5)_{1.30}]_n$. The results of this experiment support the contention that pendent phosphonium bromide salt formation is a consequence of the reaction of pendent phosphine residues with butyl bromide (generated in the exchange process) during the purification of the polymer reaction mixtures.

Synthesis of $[N_3P_3(OC_6H_4P(C_6H_5)_2\text{-}p)_3(OC_6H_4P(C_6H_5)_2(C_4H_9)^+Br^-\text{-}p)_3]$. A sample of $[NP(OC_6H_4P(C_6H_5)_2\text{-}p)_2]_3$ (0.50 g, 2.8×10^{-4} mol) was dissolved in dry benzene (100 mL), and butyl bromide (2.0 g, 1.4×10^{-2} mol) was added to this solution. The reaction mixture was refluxed for 12 h. The reaction mixture was then evaporated to dryness in a rotary evaporator. The product was isolated by recrystallization from benzene. A ^{31}P NMR spectrum of product (in THF) consisted of three resonances at +24.3, +7.9, and −6.5 ppm. These were assigned to the

phosphonium salt, the phosphazene, and the phosphine phosphorus atoms, respectively. The integrated areas of the resonances were in the ratio of 1:1:1.

Reaction of $[NP(OC_6H_5)_2]_3$ with Phenyllithium. A sample of $[NP(OC_6H_5)_2]_3$ (0.5 g, 7.0×10^{-4} mol) was dissolved in THF (100 mL). Phenyllithium (1.2 mL, 7.2×10^{-4} mol) was then added to this solution at 25 °C. The reaction mixture was stirred for 3 h and 2-propanol (2 mL, 0.023 mol) was added to deactivate the organolithium reagent. The reaction solvent was removed by a rotary evaporator, and water (25 mL) was added. The water-insoluble material was then extracted with diethyl ether (25 mL) and the diethyl ether was removed by a rotary evaporator. The diethyl ether soluble product was subjected to mass spectrometric examination. Two parent ions were detected. These were derived from $[NP(OC_6H_5)_2]_3$ (*m/e* 693) and $[NP(OC_6H_5)_5(C_6H_5)]_3$ (*m/e* 677). ^{31}P NMR spectroscopic data of this reaction mixture indicated only one resonance at +8.2 ppm (this is indicative of the presence of $[NP(OC_6H_5)_2]_3$. Thus, $[N_3P_3(C_6H_5)(OC_6H_5)_5]$ was present in small quantities only in the reaction product mixture (probably less that 5%, because the presence of more than 5% would allow for its detection by ^{31}P NMR spectroscopic methods). The presence of any amount of $[N_3P_3(C_6H_5)(OC_6H_5)_5]$ implies that the displacement of lithium phenoxide from $[NP(OC_6H_5)_2]_3$ by phenyllithium is possible and that this displacement reaction is a prospective mechanism for the cross-linking of polymers that possess *p*-lithiophenoxy and *p*-phenoxy substituent groups.

Comparison of the Metal–Halogen Exchange Reaction for Poly(*p*-bromostyrene). A sample of poly(*p*-bromostyrene) (0.5 g, 0.0060 mol) was dissolved in tetrahydrofuran (300 mL). This solution was cooled to −50 °C and *n*-butyllithium (9 mL, 0.0144 mol) was added rapidly. The reaction mixture was stirred for 6 h at −50 °C, and water (9 g, 0.5 mol) was added to deactivate the lithiated species. The reaction mixture was allowed to warm to 25 °C, the reaction mixture was concentrated by rotoevaporation, and the concentrate was added to water. The precipitated polymer was collected by filtration, dried and redissolved in tetrahydrofuran, filtered, and reprecipitated into ethanol. A reprecipitation from tetrahydrofuran into pentane was also carried out. Elemental microanalytical data implied that 15.7% *p*-bromostyrene units remained. Anal. Calcd for $[-(C_8H_8)_x-(C_8H_7Br)_y-]_{n=100}$ (x = 15.7 and y = 84.3): C, 82.50; H, 6.74; Br, 10.76. Found: C, 81.08; H, 7.22; Br, 10.77. By comparison, the metal–halogen exchange for $[NP(OC_6H_4Br\text{-}p)_2]_n$ (III) resulted in the replacement of approximately 70% of the *p*-bromophenoxy units after the same reaction time. The greater efficiency of the exchange process for poly(*p*-bromostyrene) probably reflects the fact that only one bromine atom is present per repeat unit for this polymer.

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(18) Previously reported syntheses of poly(diphenoxyphosphazene)[1] have employed metallic sodium to generate the phenoxide salt; here we report the use of sodium hydride for this purpose.

Synthesis of Alkylphosphazene High Polymers via the Polymerization of Monoalkylpentachlorocyclotriphosphazenes[1,2]

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ABSTRACT: A new class of high molecular weight poly(organophosphazenes) of general formula $[-(N{=}PCl_2)_2{-}N{=}PClR-]_n$ (VIII), where R = CH_3, C_2H_5, *n*-C_3H_7, or *n*-C_4H_9, have been prepared by the thermal polymerization of monoalkylpentachlorocyclotriphosphazenes, $N_3P_3Cl_5R$ (VII). These are among the first high molecular weight polyphosphazenes with side groups linked directly to the skeleton through C–P bonds. Hydrolytically stable, elastomeric derivatives of formula $[-N{=}P(OR')_2{-}N{=}P(OR')R-]_n$, were obtained by a replacement of the chlorine atoms in VIII with trifluoroethoxy or phenoxy groups. Bulky alkyl groups, such as *i*-C_3H_7 or *t*-C_4H_9, retard the polymerization process and sensitize the system to decomposition reactions during polymerization. The structures of the polymers were deduced by comparisons with cyclic trimeric phosphazene model compounds of formulas $N_3P_3(OCH_2CF_3)_5R$ and $N_3P_3(OC_6H_5)_5R$, where R is CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *i*-C_3H_7, or *t*-C_4H_9.

A broad range of high molecular weight poly(organophosphazenes) can be prepared by the thermal polymerization of hexachlorocyclotriphosphazene (I) to poly(dichlorophosphazene) (II), followed by nucleophilic replacement of the chlorine atoms in II by alkoxy, aryloxy, or amino substituents (Scheme I).[3-7] The resultant organophosphazene derivatives (III, IV, or V) are of fundamental and technological interest.[8-10]

Nevertheless, mechanistic and theoretical arguments can be used to show that polyphosphazenes with organic side

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