Nitro, Amino, and *N*-Amido Derivatives of Poly(methylphenylphosphazene)

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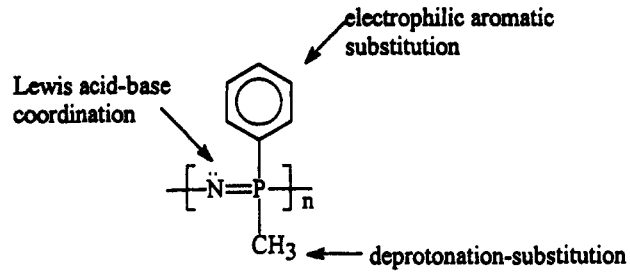
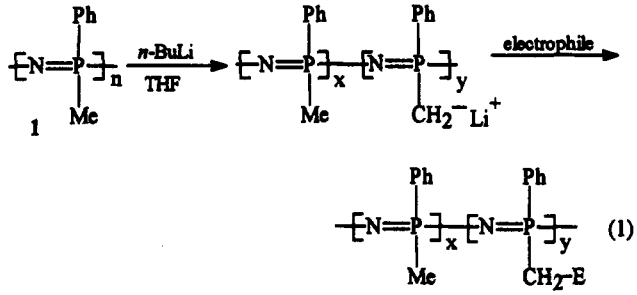
ABSTRACT: The *P*-phenyl ring in poly(methylphenylphosphazene), $[Me(Ph)PN]_n$ (1), was nitrated at the *meta* position using a mixture of nitric and sulfuric acids, producing the nitrophenyl derivatives $[Me(Ph)PN]_x[Me(3\text{-}NO_2C_6H_4)PN]_y$ (2). Between 10 and 60% of the phenyl rings were nitrated by varying the reaction times from 30 to 60 min. The nitro polymers were treated with NaOH to remove protons coordinated to the backbone nitrogen atoms and were then reduced by $NaBH_2S_3$ to the amino derivatives $[Me(Ph)PN]_x[Me(3\text{-}NH_2C_6H_4)PN]_y$ (3). Conversion to the *N*-amido-substituted polymers, $[Me(Ph)PN]_x\{Me[3\text{-}N(H)C(=O)C_2H_5](C_6H_4)PN\}_y$ (4), was accomplished by reaction of 3 with propionyl chloride in the presence of Et_3N. The new poly(phosphazenes) were characterized by elemental analysis, ^1H, ^{31}P, and ^{13}C NMR and infrared spectroscopy, size-exclusion chromatography, and differential scanning calorimetry. The unusual chemical stability of the phosphazene backbone to the rigorous chemical reactions and the effect of protonation are also discussed.

Introduction

Poly(methylphenylphosphazene), $[Me(Ph)PN]_n$ (1), which is obtained via the condensation reaction of the *N*-silylphosphoranimine, $Me_3SiN{=}P(OR)(Ph)Me$,[1] has three potential sites for chemical modification: the *P*-methyl group, the *P*-phenyl group, and the backbone nitrogen atom.



The deprotonation–substitution reactions at the *P*-methyl groups have been most thoroughly investigated. The process (eq 1) involves initial metal–hydrogen ex-



(1)

change (deprotonation) at the methyl substituents, followed by the treatment of the anion with electrophiles. This method has allowed for the synthesis of new polymers with silyl,[2a] phosphino,[2b] and bromo[2b] groups; alcohol groups;[3] carboxylate salt, carboxylic acid, and ester groups;[4] poly(styrene),[5a] poly(siloxane),[5b] and poly(methyl methacrylate)[5c] grafted copolymers; and long-chain alkyl, fluoroalkyl,[6] and polyether[7] groups.

Recently we have shown that the backbone nitrogen atoms in poly(methylphenylphosphazene) and poly(dimethylphosphazene), $[Me_2PN]_n$, have a pronounced tendency to coordinate to various Lewis acids (e.g., $LiBF_4$, $AgBF_4$, and HCl).[8] Treatment of the proton complexes with K_2CO_3 and the silver complexes with NaCl resulted in recovery of the parent polymers. The ^{31}P NMR spectra of the lithium complexes showed the expected two resonances at 213 K which coalesced to a single resonance at 300 K. This is indicative of a facile pathway for lithium transport along the polymer backbone or between polymer chains. The backbone configuration of the nitrogen atoms with a variety of other moieties is under investigation.

In this paper, we report the first successful reactions of the third reactive site in poly(alkyl/arylphosphazenes), i.e., the P–C-bonded aromatic groups. Electrophilic aromatic substitution reactions of the phenyl groups in $[Me(Ph)PN]_n$ were used to synthesize new nitro-substituted poly(phosphazenes), 2 (Scheme 1). The nitration, which is accomplished with HNO_3/H_2SO_4, is discussed with respect to the concurrent protonation of the backbone in this acidic medium. Subsequent reduction of the nitro groups to amines and conversion to *N*-amido derivatives are also reported.

The electrophilic aromatic substitution of aryl groups attached to the poly(phosphazene) backbone by P–O or P–N linkages rather than P–C bonds has been reported in both solution and on immobilized surfaces by Allcock and co-workers.[9,10] Poly(bisphenoxyphosphazene), $[(PhO)_2PN]_n$, coated on the surface of alumina, was nitrated with HNO_3/H_2SO_4. The nitro-substituted polymer was not, however, isolated and characterized. Instead, the nitro groups were converted to amines that were then used to immobilize enzymes such as trypsin on the alumina surface.[9] More recently, the sulfonation of both aryloxy- and arylamino-substituted phosphazene cyclic trimers, polymers, and cross-linked polymer films was reported.[10] Fully characterized nitroaryloxy-substituted polymers poly[(4-nitrophenoxy)phenoxyphosphazene] were prepared by an alternate procedure involving the direct substitution of $[Cl_2PN]_n$ with $NaOC_6H_4\text{–}NO_2$ and NaOPh. The sequential reduction of the nitro groups to amino groups and appropriate diazotization reactions resulted in the covalent attachment of neurotransmitters such as

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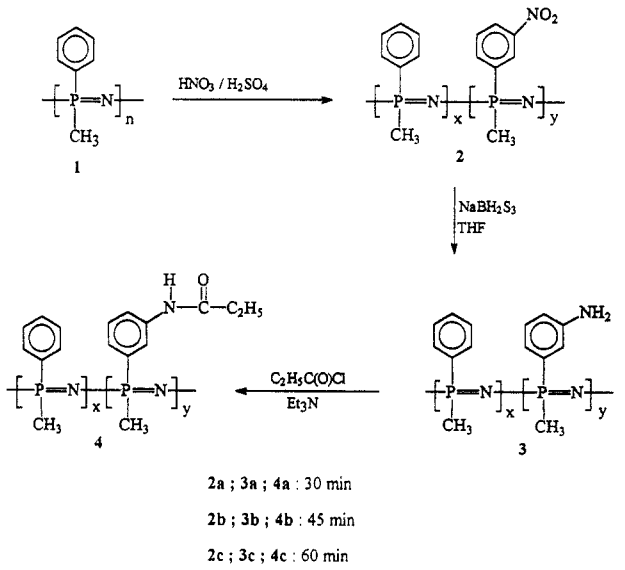
Scheme 1



dopamine to the poly(phosphazene).[11] The biological activity of polymer-bound trypsin enzyme and dopamine was not inhibited by attachment to the phosphazene,[9,11] thus demonstrating the synthetic utility of aminoaryl-substituted poly(phosphazenes).

Results and Discussion

Considering the general versatility of electrophilic aromatic substitution reactions, the phenyl groups in $[Me(Ph)PN]_n$ appear to be an ideal derivatization site. Nonetheless, many simple substitution reactions of the polymer are hampered by the reactivity of other sites in the poly(phosphazene). For example, we have found that attempts to acylate the phenyl ring using catalysts such as $AlCl_3$ are complicated by coordination of the backbone as evidenced by downfield shifts in the ^{31}P NMR spectra[8] and by decreased molecular weights that result from extensive chain degradation. Nitration of the ring can, however, be accomplished using the well-known reaction medium of a mixture of concentrated nitric acid/sulfuric acid (1:2, v/v). Initially the reactions were examined at ambient temperature and at 50 °C, but, while it was not clear that chain degradation occurred at these temperatures, the exothermic nature of the solubilization/reaction indicated that cooling to 0 °C was appropriate. Using these conditions, reaction times between 15 and 150 min were examined. The parent polymer 1 has limited solubility in both the HNO_3 and H_2SO_4 acids, but as the reaction progressed larger amounts of the polymer dissolved in the reaction medium. Reaction times of 30, 45, and 60 min (Scheme 1) were selected as optimum times based on GPC, elemental analysis, and NMR spectroscopic data.

The nitro derivatives **2a–c** were isolated by pouring the reaction mixture onto ice followed by filtration of the aqueous mixture. The polymers were further purified by precipitation from CH_2Cl_2 solutions into hexane. The ^{31}P NMR spectra of polymers **2** at this point showed multiple peaks between 0 and 5 ppm (Figure 1a). The downfield shifted signals in the ^{31}P NMR spectra suggested that some of the nitrogen lone pairs in the PN backbone of the polymer are protonated. Further evidence for backbone protonation comes from the observation of an IR signal at 2679 cm^{-1} which is attributed to an N–H stretching frequency.[12] Similar ^{31}P NMR chemical shifts and IR spectroscopic signals have been observed when the parent

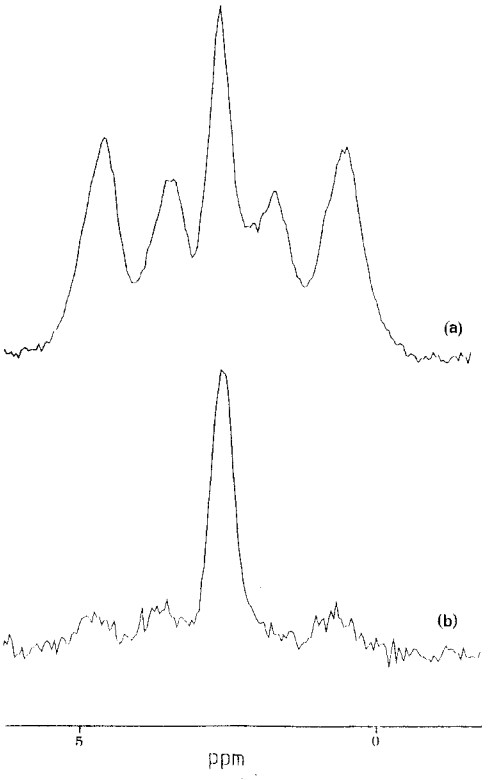


Figure 1. ^{31}P NMR spectra of **2a** (a) before and (b) after treatment with NaOH.

polymer $[Me(Ph)NP]_n$, 1, is partially protonated[8] and in the self-protonated zwitterionic form of the carboxylic acid derivatives.[4] The protonation of the backbone also explains some inconsistent elemental analysis data for various experiments. These data become more reasonable when coordination of protons and the corresponding anions (e.g., SO_4^{2-}) is taken into consideration.

The removal of protons from the backbone in the nitro derivatives **2** was somewhat difficult, due to the strong basicity of the polymer backbone. When treatment of THF solutions of the polymers **2** with excess Et_3N for several hours failed to give analytically and spectroscopically pure samples, THF solutions of the polymers were ultimately stirred for 6–10 h with very concentrated solutions of NaOH. This was followed by purification by precipitations from THF into water and then from THF into hexane. The ^{31}P NMR spectrum for polymer **2a** after deprotonation with NaOH (Figure 1b) shows only the expected single signal at δ 2–3 which compares favorably with that for **1** (δ 2). The ^{31}P spectra of **2b** and **2c** were similar. The ^{1}H and ^{13}C NMR spectra of the nitro derivatives remained the same before and after deprotonation of the backbone. Elementary analyses of polymers **2**, however, were greatly improved and completely reproducible following the rigorous treatment with strong bases. From the elemental analysis data, the percent substitution of the phenyl groups for polymers **2a–c** was determined to be approximately 10, 30, and 60% for the 30-, 45-, and 60-min reactions, respectively. It is particularly noteworthy that these transformations were accomplished without chain degradation (see below).

Once purified the nitro-substituted polymers **2** were soluble in THF, CH_2Cl_2, and $CHCl_3$. Polymer **2a** was soluble in toluene, but **2b** and **2c** were only moderately soluble presumably due to the higher incorporation of polar nitro groups. They were slightly yellow in color and were typically isolated as powders which could be solution cast as brittle films.

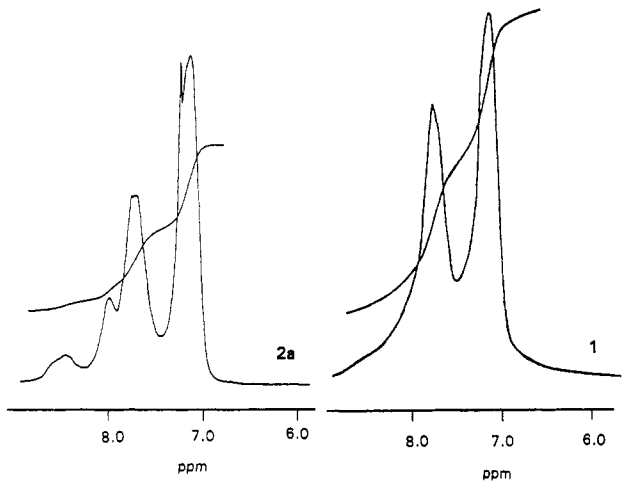


Figure 2. Aromatic region of ^1H NMR spectra of the parent polymer $[Me(Ph)PN]_n$ (1) and the nitro derivative **2a**.

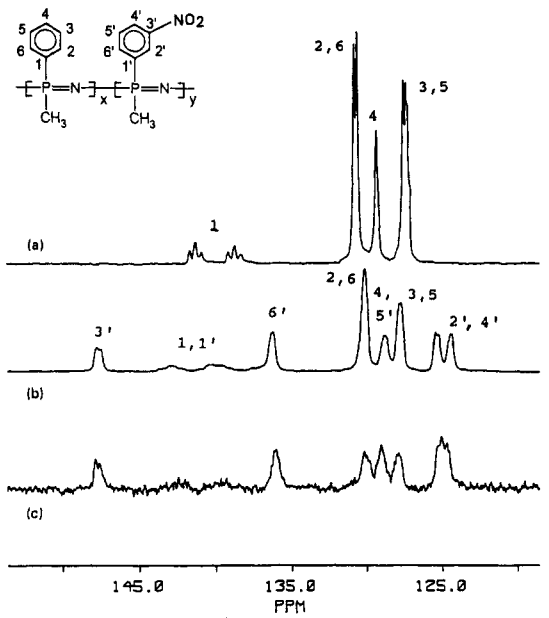


Figure 3. Aromatic region of the ^{13}C NMR spectra of (a) the parent polymer $[Me(Ph)PN]_n$ (1), (b) the nitro derivative **2a**, and (c) the nitro derivative **2b**.

The orientation of the nitro group in the phenyl ring of the polymer was found to be at the 3 (*meta*) position by overtone bands in the 1667–2000-cm^{-1} region of IR spectra.[13] A comparison of the aromatic regions of the ^1H NMR spectra of the parent polymer 1 and the nitro derivative **2a** (Figure 2) clearly shows additional signals for the protons of the nitrated ring at δ 7.2 (5′), 7.8 (6′), 8.0 (4′), and 8.5 (2′). These new signals are consistent with the relatively complicated spectra associated with *meta* substitution as opposed to *ortho* or *para* substitution. This parallels the sulfonation reactions of the phenyl ring in hexaphenylcyclotriphosphazene ($N_3P_3Ph_6$) reported by Allcock[10] wherein the substitution was also at the *meta* position. In the same report it was found that aryloxy rings on phosphazenes (both trimers and polymers) underwent sulfonation at the 4 (*para*) position or at 3 (*meta*) position if the *para* position was blocked by an alkyl substituent. These results are consistent with the strong electron-withdrawing effect of the protonated phosphazene unit.[14]

Further confirmation of *meta* substitution was provided by the ^{13}C NMR spectra. Figure 3 illustrates the changes in the aromatic region of the ^{13}C NMR spectra upon conversion of the parent polymer 1 to the nitrated polymers **2a** and **2b**. New signals that are consistent with *meta* substitution are clearly observed at δ 124.5–125.5 (carbons 2′, 4′), 136.3 (6′), and 147.5 (3′) for both **2a** and **2b**.[15] These signals are more prominent for the polymer **2b** (Figure 3c) which confirms the increased degree of substitution that results from the 45-min reaction time. Carbon 5′ (δ 129) is more visible in the spectrum of **2b**, and significant decreases in the signals for unsubstituted phenyl rings at δ 130.8 (carbons 2, 6) and 127.4 (3, 5) are also observed.

The nitration of the parent polymer 1 with the nitronium salt NO_2BF_4 in fluorosulfonic acid[16] was also investigated as a possible means of optimizing the degree of substitution. However, this resulted in complications such as the lack of complete solubility of the product in THF and chlorinated solvents. Although the IR spectrum of the product after precipitation showed appropriate peaks for the NO_2 groups at 1530 and 1350 cm^{-1}, this synthetic route was not pursued any further because of the difficulty in handling the reagents, unsuccessful attempts to deprotonate the polymers, and ^{31}P NMR spectra that suggested that chain degradation had occurred.

The tendency of the backbone nitrogen atoms to coordinate to Lewis acids and transition-metal compounds limited our ability to use various reducing agents to reduce the nitro groups and necessitated greater than stoichiometric amounts of the reagents for complete reactions. Attempted reduction reactions with $Fe/FeSO_4$, $Cu(acac)_2$, Sn/HCl, and Pt/H_2 resulted in incomplete reduction and generally were irreproducible. Since many of these catalysts were investigated early in this study before it was clear that the rigorously basic workups were necessary to completely deprotonate the backbone, it is possible that these reactions were also complicated by protonated backbone nitrogen atoms. The reduction of the nitro groups in **2** was successfully achieved by reaction with $NaBH_2S_3$ in THF under reflux (Scheme 1). Best results were obtained when $NaBH_2S_3$ was freshly made prior to the reduction reaction according to the literature procedure.[17] The purification and workup of the amino-substituted polymers **3** also involved basic conditions since the reaction mixture was hydrolyzed with a 10% HCl solution upon completion. This is particularly important for the amine derivatives since these materials became partially insoluble in THF and chlorinated solvents if heated while the backbone was protonated. Even with the basic workup and drying at ambient temperatures, polymers **3** dissolved more sluggishly in THF and chlorinated solvents than the nitro derivatives **2**. Infrared and ^{13}C NMR spectra of **3** confirmed that all the nitro groups were reduced to the amino groups. The N–O stretching bands at 1350 and 1530 cm^{-1} in **2** were replaced by the N–H bending bands at 1598 and 1618 cm^{-1} in the IR spectra of polymer **3**.[13] In the phenyl region of the ^{13}C NMR spectra (Figure 4c), the *meta* (3′) carbon resonance shifted from δ 147.5 for **2** to δ 145.8 for **3** (Figure 4b) while carbon 6′ moved from δ 136.3 to 120.7.[15]

Conversion of the amine derivative **3** to the *N*-alkylamido derivatives **4** was accomplished by reaction with propionyl chloride in the presence of Et_3N in THF at room temperature. In the ^{13}C NMR spectra for **4** the *meta* carbon (3′) was observed at δ 137.8, with carbons 2′, 4′, and 6′ also moving as expected[15] (Figure 4c). The carbonyl carbon was observed at δ 172.2 in the ^{13}C NMR spectra, and the C=O stretch was observed at 1670 cm^{-1} in the IR spectrum. These derivatives were prepared to increase the alkyl to aryl ratios in the ^1H NMR spectra. This facilitated the use of integration of these regions to approximate the fraction of phenyl groups that were

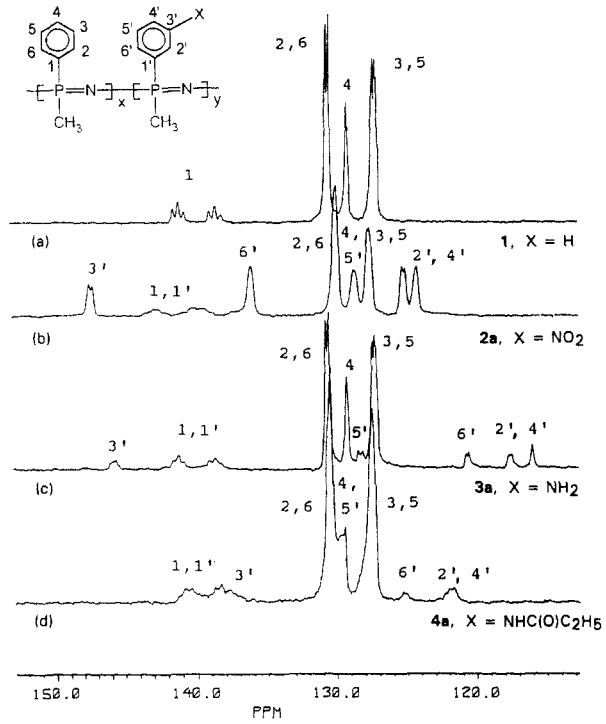


Figure 4. Aromatic region of the ^{13}C NMR spectra of (a) the parent polymer 1, (b) the nitro polymer 2c, (c) the amino polymer 3a, and (d) the amido polymer 4a.

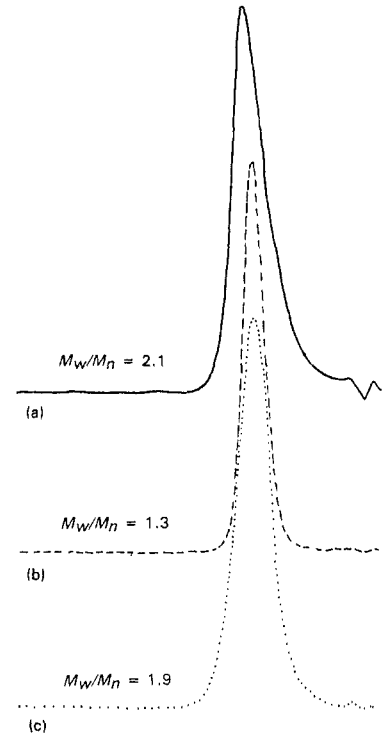


Figure 5. Size-exclusion chromatograms for (a) the parent polymer 1, (b) the nitro polymer 2a, and (c) the amino polymer 3a.

substituted in the original nitration of the parent polymer 1. As shown for **4a–c** in Table 1, the percent substitution obtained by integration was 9, 23, and 53%, respectively. This is remarkably close to the 10, 30, and 60% values obtained from elemental analyses. A more important feature of each series is the agreement in the degree of phenyl substitution values for the nitro, amino, and amido polymers as determined by elemental analyses. For example, in the nitro polymer **2c** from the 60-min nitration reaction, ca. 60% of the phenyl groups were substituted. In the amino **3c** and amido **4c** polymers, which were made from the same batch of **2c**, elemental analyses data were also consistent with substitution of 60% of the phenyl groups.

Throughout these transformations, the phosphazene polymer backbone did not appear to undergo chain degradation reactions as supported by similar peak positions in size-exclusion chromatograms (SEC) (Table 1). However, the molecular weight distributions (M_w/M_n) varied somewhat throughout the series of derivatives. The M_w/M_n for the nitro derivatives were lower than for either the parent polymer or the amino and *N*-amido derivatives. Figure 5 illustrates the changes in M_w/M_n for the polymer transformations **1** → **2a** → **3a**. The narrowing of the SEC peak for **2a** (M_w/M_n = 1.3) may result from variations in apparent molecular size due to the presence of polar NO_2 groups, unusual interactions of this polymer with the SEC column, and/or altered solution effects. The molecular weight distributions for **1** (M_w/M_n = 2.1), **3a** (M_w/M_n = 1.9), and **4a** (M_w/M_n = 2.1) were, however, very similar which indicates that the low value of M_w/M_n for the nitrated polymers was not due to chain degradation or other variations in the length of the polymer backbone. The same trend was observed for the 30% ("**b**" series) and 60% ("**c**" series) as shown in Table 1.

The glass transition temperatures (T_g) were determined using differential scanning calorimetry for the derivatized polymers and were generally higher than the T_g value for the parent polymer. This is expected with the incorporation of more polar nitro, amino, and amido groups. Derivatives **2b**, **3b**, and **4b** exhibited a single transition, while two transitions were observed for the other derivatives (i.e., the "**a**" and "**c**" series). The lower T_g values for the "**a**" and "**c**" series were similar to that of the parent polymer (37 °C), and the higher values corresponded to the substituted polymers. This may be a result of the partial insolubility of parent polymer 1 in the HNO_3/H_2SO_4 reagents in the initial nitration step which could result in either block type reactions or in a blend of unreacted parent polymer 1 and nitrated derivatives. The T_g values for the derivatives followed the expected trends, with the nitro derivatives having the lowest values (48–59 °C). The amino derivatives, where hydrogen bonding is possible, had the highest values (79–84 °C).

In summary, the nitration of the phenyl substituents in poly(methylphenylphosphazene) and subsequent reduction of the nitro groups is a straightforward, easily controlled process leading to well-defined, soluble poly(alkyl/arylphosphazene) derivatives. The complete chemical characterization of these new polymers complements the previous surface reactions of poly(bisphenoxyphosphazene) and serves as a model for surface reactions of phenyl groups in the poly(alkyl/arylphosphazenes). The new reactive sites provide access to new types of organic derivative chemistry for the poly(alkyl/arylphosphazenes), such as diazotization reactions of the amino groups.

Experimental Section

Materials. Poly(methylphenylphosphazene), $[Me(Ph)PN]_n$ (1), was prepared by the published procedure[1] and was dried under vacuum at 50 °C for 18 h. Tetrahydrofuran and propionyl chloride (Aldrich) was freshly distilled from Na/benzophenone and BaO, respectively, prior to use. For reduction of the nitro groups, Lalancette's reagent was prepared according to the literature procedure.[17] Sulfuric acid, nitric acid, sodium borohydride, and sulfur powder were obtained from commercial sources.

Equipment. The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on an IBM WP-200SY FT NMR spectrometer in $CDCl_3$. Positive

Table 1. Analytical, Size-Exclusion Chromatography (SEC), and Thermal (DSC) Data

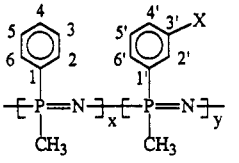
polymer	% yield	analyses			% substitution[b,c]	M_w[d,e]	T_g, °C
		% C[a]	% N[a]	% H[a]			
2a	51	59.78 (59.37)	10.58 (10.88)	5.92 (5.62)	10	103 000 (1.3)	33, 48
2b	61	54.35 (55.82)	12.79 (12.09)	4.63 (5.15)	30	103 000 (1.4)	54
2c	55	51.64 (51.23)	13.11 (13.66)	4.81 (4.54)	60	117 000 (1.2)	42, 59
3a	51	59.50 (60.65)	11.54 (11.11)	6.04 (5.89)	10	98 000 (1.9)	33, 79
3b	43	58.34 (59.37)	13.02 (12.86)	5.92 (5.91)	30	85 000 (2.6)	84
3c	54	56.44 (57.54)	15.55 (15.34)	5.84 (5.93)	60	83 000 (2.2)	38, 81
4a	56	60.01 (60.79)	11.12 (10.68)	6.04 (5.94)	10 (9)	73 000 (2.1)	42, 69
4b	49	59.34 (59.89)	11.32 (11.49)	6.53 (6.04)	30 (23)	71 000 (1.9)	70
4c	53	58.64 (58.80)	12.16 (12.47)	6.31 (6.17)	60 (53)	95 000 (2.1)	34, 79

[a] Calculated values in parenthese are based on % substitution. [b] % substitution = $(y/x + y)100$. [c] Values in parentheses were determined by integration of the ^{1}H NMR spectra. [d] The value for the parent polymer 1 is 79 000. [e] Molecular weight distributions (M_w/M_n) are in parentheses.

Table 2. Representative NMR (ppm) and IR (cm^{-1}) Spectroscopic Data[a,b]

polymer	^{1}H NMR	^{13}C NMR	^{31}P NMR	IR
2	0.9–1.4 (CH_3), 7.2 [H(3,4,5,5′)], 7.8 [H(2,6,6′)], 8.0 [H(4′)], 8.5 [H(2′)]	147.5 [C(3′)], 140.3–143.0 [C(1,1′)], 136.3 [C(6′)], 130.1 [C(2,6)], 128.8 [C(4,5′)], 127.8, 127.7 [C(3,5)], 124.5–125.5 [C(2′,4′)], 20.7–23.6 (P–CH_3)	2.2	1270 (PN), 1350 (NO_2), 1530 (NO_2)
3	1.0–2.2 (CH_3), 7.4 [H(3,4,5,2′,4′)], 8.0 [H(2,6,5′,6′)]	145.8 [C(3′)], 138.7–141.3 [C(1,1′)], 130.8 [C(2,6), $^1J_{PC}$ = 10], 129.3 [C(4)], 128.5 [C(5′)], 127.4 [C(3,5), $^1J_{PC}$ = 7.5], 120.8, 120.6 [C(6′)], 117.7 [C(2′)], 116.1 [C(4′)], 20.7–23.6 (P–CH_3)	2.5	1270 (PN), 1598 (NH_2), 1618 (NH_2)
4	0.9–1.8 (CH_3; C–CH_3), 2.3 (CH_2), 7.4 [H(3,4,5,2′,5′)], 8.0 [H(2,6,5′,6′)]	172.2 (C=O), 138.3–142.0 [C(1,1′)], 137.8 [C(3′)], 130.5 [C(2,6)], 129.4 [C(4,5′)], 127.6 [C(3,5)], 125.3 [C(6′)], 121.7 [C(2′,4′)]	2.8	1265 (PN), 1670 (C=O)

[a] Chemical shifts downfield from Me_4Si for ^{1}H and ^{13}C NMR spectra and from H_3PO_4 for ^{31}P NMR spectra. Solvent $CDCl_3$. [b] The numbering system for phenyl groups in proton and carbon spectra are as shown:



^{1}H NMR and ^{13}C NMR chemical shifts are downfield from the external reference Me_4Si, while positive ^{31}P NMR shifts are downfield from the external reference H_3PO_4. Elemental analyses were performed on a Carlo Erba Strumentazione CHN Elemental Analyzer 1106. The size-exclusion chromatography (SEC) measurements were performed on a Waters Associates GPC instrument with a Maxima data handling system using 500-, 10^4-, 10^5-, and 10^6-Å μ-Styragel columns. The SEC operating conditions consisted of a mobile phase of THF containing 0.1% (n-Bu)$_4$N$^+$Br$^-$, a flow rate of 1.5 mL/min, a temperature of 30 °C, and a sample size of 0.05 mL of a 0.1% solution. The system was calibrated with a series of narrow molecular weight polystyrene standards in the range of ca. 10^3–10^6. IR spectra were recorded as KBr pellets on a Perkin-Elmer 283 infrared spectrometer. Differential scanning calorimetry (DSC) measurements were made on a DuPont Model 910 instrument equipped with a TA 2000 data station. Measurements were made under nitrogen against an aluminum reference from 0 to 150 °C using ca. 10-mg samples and heating at a rate of 10 °C/min. Each experiment was repeated at least three times on the same sample.

Synthesis of Nitro Derivative 2a. Concentrated nitric acid (10 mL) and sulfuric acid (40 mL) were mixed and cooled in an ice bath. Finely powdered poly(methylphenylphosphazene) (1; 1.0 g, 7 mmol) was added to the acid solution, and the reaction mixture was stirred for 30 min. The reaction was quenched by pouring the mixture onto ice, and the precipitated polymer was collected by filtration. The polymer was dissolved in THF to make a dilute solution, and ca. 10–15 mL of a 20% sodium hydroxide solution was added to the THF solution of the polymer. After stirring for 15–20 h, the polymer was precipitated in a large excess of water. The polymer was collected by filtration and then reprecipitated from THF into water. Further purification was achieved by precipitating the polymer from a toluene solution into hexane. The product was dried in a vacuum oven at 60 °C for 48 h. Isolated yields and other characterization data are listed in Table 1. NMR and IR spectroscopies are given in Table 2.

Synthesis of Nitro Derivatives 2b and 2c. The procedure for the synthesis is the same as that reported for polymer **2a**. Washing with a 20% NaOH solution followed by precipitation into water yielded a polymer that exhibited multiple peaks in the ^{31}P NMR spectrum. The polymer derivatives had no appreciable solubility in nonpolar solvents such as benzene or toluene. Purification was achieved by adding a concentrated NaOH solution (1 g of NaOH in 2–4 mL of H_2O) to a dilute solution of the polymer in THF (1 g of polymer in ca. 25–50 mL of THF) and stirring the mixture for 20–30 h. The polymer was recovered by precipitation into a large excess of water. Further purification was done by precipitating the polymer from a THF solution into hexane. This procedure was repeated until the ^{31}P NMR showed no change (usually two to three times per sample). The product was dried in a vacuum oven at 60 °C for 40–50 h.

Synthesis of Amine Derivatives 3a–c. A mixture of 1.2 g of $NaBH_4$ (30 mmol) and 3.2 g of sulfur (10 mmol) was treated with 25 mL of freshly distilled THF with stirring in a 250-mL round-bottomed flask equipped with a condenser. The reaction was exothermic, and a brisk evolution of gas occurred. The reaction flask was cooled in an ice–water bath. After 1 h of stirring, the solvent was removed under vacuum at room temperature and the product was washed two times with anhydrous ether. The product was dried in a vacuum oven for 18 h with adequate precautions to exclude air and oxygen. The sulfurated borohydride ($NaBH_2S_3$, Lalancette's reagent)[17] thus obtained is then suspended in 45 mL of dry THF. A THF solution of the nitrated polymer **2** (2.92 g, 17 mmol) was added to the $NaBH_2S_3$ solution, and the reaction mixture was stirred and refluxed for 24–30 h. The reaction mixture was hydrolyzed with a 10% HCl solution until a pH of 1 was maintained. After stirring this solution for 12 h, the precipitated sulfur was removed by filtration and ca. 5–10 mL of a 20% NaOH solution was added. This mixture was allowed to stir for 24–30 h. The polymer was isolated by pouring the mixture into a large excess of water. Further purification

was achieved as reported above for **2**. The polymer was dried in a vacuum oven without heat for 40–60 h.

Synthesis of Amide Derivatives 4a–c. A solution of 0.65 g of the amine polymer **3** (5.3 mmol) in 10 mL of THF was treated with 2.0 mL of Et_3N and 0.7 mL of $C_2H_5C(O)Cl$ (8 mmol) at 0 °C. The reaction was stirred for 4 h at room temperature and quenched by pouring into water. The polymer was isolated by filtration, redissolved in THF, treated with a 20% NaOH solution (2 mL), and then precipitated into water. Further purification was done as reported in the earlier procedures.

Yields (Table 1) of the polymers are based on the degree of substitution determined from the elemental analyses. The degree of substitution was also determined from integration of the ^1H NMR spectra of the amide derivatives **4** and is reported in parentheses. Elemental analyses, differential scanning calorimetry, and SEC molecular weight data are also listed in Table 1.

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