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Functionalization of Phosphazenes. 1. Synthesis of Phosphazene Materials Containing Hydroxyl Groups

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ABSTRACT: In this paper we report the synthesis of 4-hydroxyphenol (hydroquinone)-substituted phosphazene materials, i.e., hexakis(4-hydroxyphenoxy)cyclophosphazene and poly[bis(4-hydroxyphenoxy)phosphazene], by reaction of 4-methoxyphenoxy-substituted cyclo- and polyphosphazenes with an excess of BBr_3. An alternative method is based on a Pd-catalyzed hydrogenation under pressure of other phosphazene substrates bearing 4-(benzyloxy)phenoxy substituents. In the case of cyclic phosphazene derivatives, both these reactions take place very smoothly, while a dramatic decrease of the molecular weight is observed for the phosphazene high polymers during the reaction of poly[bis(4-methoxyphenoxy)phosphazene] with boron tribromide and during the hydrogenation process of the poly[bis(4-(benzyloxy)phenoxy)phosphazene]. In the case of poly[bis(4-methoxyphenoxy)phosphazene], the deblocking reaction of the methoxy group can be modulated to introduce in the phosphazene substrate a predictable amount of OH groups. The successive functionalization of the produced free hydroxyl functions in the phosphazene oligomers and polymers is also discussed by considering the acetylation of these groups as a prototype process for the phosphazene substrates.

Introduction

The introduction of chemical functionalities in preformed polymeric materials to synthesize new macromolecules showing different physical and chemical properties is a process of paramount importance in polymer chemistry.[1] Many technologically important functionalizations, such as sulfonation,[2] nitration,[3] chloromethylation,[4] etc., are currently exploited, for example, on styrene–divinylbenzene resins, to produce polymeric matrices of industrial interest.

In the case of poly(organophosphazenes) (POP), the chemical modification to produce new phosphazene macromolecules is very attractive.[5] However, the synthetic method used for the preparation of these materials (based on the nucleophilic replacement of the reactive chlorines in the poly(dichlorophosphazene) [$(NPCl_2)_n$] with suitable substituents[6,7]), although very flexible and enabling the synthesis of a large number of different macromolecules,[8] is not very effective when groups of low basicity and/or high steric hindrance are used in the process.[9]

The preparation of functionalized POP containing free "X" functionalities can be, in principle, achieved in three ways according to Scheme I: (a) reaction of $(NPCl_2)_n$ with the nucleophile "Y" to prepare $[NP(Y)_2]_n$, followed by modification of this preformed polymer by introduction of "X" functions on the side "Y" substituent using convenient chemical methods (pathway A) (this strategy is completely analogous to that already described to modify organic polymers,[10] and it can be demonstrated that most of the functionalization reactions commonly used for these materials work quite satisfactorily also when applied to POP[11,12]); (b) direct nucleophilic substitution of the reactive chlorines in $(NPCl_2)_n$ with bi- or multifunctional reagents "Y–X" that have only the "Y" group able to react with $(NPCl_2)_n$, the other function "X" remaining unaffected during this process (pathway B);[13] (c) reaction of poly(dichlorophosphazene) with a nucleophilic reagent "Y–X–P" (in which a second nucleophilic functionality "X" is masked by a suitable protecting group "P") to obtain the polymer $[NP(Y–X–P)_2]_n$, followed by a convenient deprotection reaction to $[NP(Y–X)_2]_n$ (pathway C).[14]

The last two methods have been applied successfully in the past; it seems, however, that the preparative strategy reported in pathway C of Scheme I has a tremendous potential which has not been entirely explored so far. We decided, therefore, to adopt this technique to produce new, very interesting, phosphazene materials, taking into consideration, as a possible substituent on the phosphazene backbone, 4-hydroxyphenol (hydroquinone).

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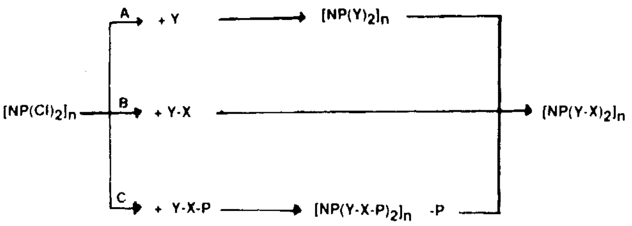
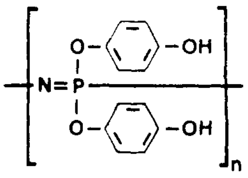
Scheme I



In this paper, we report the synthesis of poly[bis(4-hydroxyphenoxy)phosphazene] (OHPOP), obtained from



poly[bis(4-methoxyphenoxy)phosphazene] [(PBMPP), $[NP(OC_6H_4OCH_3)_2]_n$] or from poly[bis(4-(benzyloxy)phenoxy)phosphazene] [(PBBOPP), $[NP(OC_6H_4OCH_2C_6H_5)_2]_n$] through deprotection of the OH groups present in these polymers by standard organic reactions.[15,16] We also mention some synthetic exploratory work on the low molecular weight cyclic compound hexakis(4-hydroxyphenoxy)cyclophosphazene [(OHT), $[NP(OC_6H_4OH)_2]_3$].[17]

A series of chemical modifications carried out on the hydroxyl groups of these phosphazenes are reported elsewhere.[18,19]

Experimental Section

Equipment. ^{31}P, ^{1}H, and ^{13}C NMR spectra were obtained with a Varian FT 80 NMR spectrometer and a Varian Gemini 300 spectrometer, respectively.

Infrared spectra were recorded with a Perkin-Elmer Model 297 spectrophotometer.

The weight-average molecular weights (M_w) of the polymers were measured by light scattering using a Sophica spectrogoniodiffusimeter.[20]

Hydrogenation reactions were performed using a Parr hydrogenator apparatus at 2 atm of hydrogen pressure in the presence of 10% palladium supported on carbon as a catalyst.

T_g values of the polymers were measured with a Mettler DSC 30 differential scanning calorimeter.

Materials. Tetrahydrofuran (THF), dioxane, dichloromethane, and pyridine were C. Erba analytical solvents and were anhydrified when necessary according to standard procedures.[21] Sodium hydride 60% oil dispersion and acetic anhydride (Aldrich) were used as received. 4-Methoxyphenol and 4-(benzyloxy)phenol (Aldrich) were anhydrified prior to use by distillation of the toluene/water azeotrope. Hexachlorocyclophosphazene [$(NPCl_2)_3$] was purchased from Shin Nisso Kako (Japan) and purified by vacuum sublimation until a constant melting point (113 °C)[22] was obtained. Poly(dichlorophosphazene) [$(NPCl_2)_n$] was obtained by ring-opening polymerization of hexachlorocyclophosphazene at 250 °C under vacuum[6,7] and was freed from the unpolymerized trimer by vacuum sublimation at 60–70 °C.

Synthesis of Cyclo- and Polyphosphazenes. All reported syntheses were carried out under a flow of dry nitrogen and with anhydrous solvents.

Hexakis(4-methoxyphenoxy)cyclophosphazene[23] (MPT, $[NP(OC_6H_4OCH_3)_2]_3$ (1)) and poly[bis(4-methoxyphenoxy)phosphazene][24,25] (PBMPP, $[NP(OC_6H_4OCH_3)_2]_n$ (3)) were prepared as reported. The weight-average molecular weight obtained for PBMPP was 2 500 000.

Synthesis of Hexakis(4-(benzyloxy)phenoxy)cyclophosphazene (BOPT, $[NP(OC_6H_4OCH_2C_6H_5)_2]_3$ (2)). A suspension of 20.00 g (5.74×10^{-2} mol) of hexachlorocyclophosphazene, 22.99 g (0.57 mol) of NaH 60% oil dispersion, and 1.5 g of tetrabutylammonium bromide in 200 mL of THF was treated with 115.1 g (0.57 mol) of 4-(benzyloxy)phenol in 250 mL of the same solvent. The addition was carried out dropwise, waiting each time for hydrogen evolution. The reaction mixture was successively refluxed for 48 h, cooled to room temperature, and ultracentrifuged at 8000 rpm to separate the liquid from the solid. The liquor was finally evaporated to dryness with a rotovap. The solid brown paste obtained in this way was treated successively with methanol to obtain a white powder which was isolated by filtration, thoroughly washed with water and methanol, and dried. The trimer was purified by multiple crystallizations from 50% THF/CH_3OH mixtures: yield 55.00 g (72.00%); analytical data are given in Table I.

Synthesis of Poly[bis(4-(benzyloxy)phenoxy)phosphazene] (PBBOPP, $[NP(OC_6H_4OCH_2C_6H_5)_2]_n$ (4)). A suspension of 19.15 g (0.48 mol) of NaH 60% oil dispersion and 2 g of tetrabutylammonium bromide in 150 mL of dioxane was treated dropwise with 4-(benzyloxy)phenol (103.60 g (0.51 mol)) in 300 mL of the same solvent. After hydrogen evolution ceased, the mixture was refluxed overnight.

The suspension was successively filtered under nitrogen, via a Schlenk technique, directly into a solution of poly(dichlorophosphazene) (15 g (0.13 mol)) in 200 mL of dioxane and was refluxed for 48 h. The reaction mixture was cooled to room temperature and poured into a large excess of water. The recovered white polymer was successively purified by multiple dissolutions in THF and reprecipitations in water (three times), methanol (twice), and *n*-heptane (once): yield 39.00 g (69.00%) of polymer; $M_w = 2\,500\,000$; $T_g = +31$ °C; analytical data are given in Table I.

Synthesis of Hexakis(4-hydroxyphenoxy)cyclophosphazene (OHT, $[NP(OC_6H_4OH)_2]_3$ (5)) from Hexakis(4-methoxyphenoxy)cyclophosphazene ($[NP(OC_6H_4OCH_3)_2]_3$ (1)). A solution of 1.74 mL (1.8×10^{-2} mol) of boron tribromide in anhydrous CH_2Cl_2 (30 mL) was treated dropwise with a solution of 2.18 g (3×10^{-3} mol) of hexakis(4-methoxyphenoxy)cyclophosphazene in anhydrous CH_2Cl_2 (50 mL). The reaction mixture was stirred at room temperature for 3 h and successively poured into 50 mL of water. A white solid was collected by filtration, washed several times with water, and dried: yield 1.86 g (96%); analytical data are given in Table I.

Synthesis of Hexakis(4-hydroxyphenoxy)cyclophosphazene (OHT, $[NP(OC_6H_4OH)_2]_3$ (5)) from Hexakis(4-(benzyloxy)phenoxy)cyclophosphazene ($[NP(OC_6H_4OCH_2C_6H_5)_2]_3$ (2)). A 500-mL Parr hydrogenator was charged with 2.7 g (2×10^{-3} mol) of hexakis(4-(benzyloxy)phenoxy)cyclophosphazene in 100 mL of 1/1 THF/CH_3OH and 0.5 g of carbon supporting 10% Pd. This solution was stirred 16 h under 2 atm of hydrogen pressure, filtered successively through Celite, and evaporated under reduced pressure. The obtained white solid was washed with 70 mL of $CHCl_3$, filtered again, and dried: yield 1.5 g (95%) of a trimer which presents the same characterization data described in the previous example.

Synthesis of Hexakis(4-(acetyloxy)phenoxy)cyclophosphazene ($[NP(OC_6H_4OCOCH_3)_2]_3$ (6)). A solution of 0.790 g (1×10^{-3} mol) of hexakis(4-hydroxyphenoxy)cyclophosphazene in 2 mL of dry pyridine was treated with 1.2 mL (1.3×10^{-2} mol) of acetic anhydride. After 2 h of stirring, the reaction mixture was diluted with 50 mL of dichloromethane and extracted with 5% aqueous HCl (2 × 20 mL) and with a saturated solution of $NaHCO_3$ (2 × 20 mL). The organic layer was dried over anhydrous Na_2SO_4, filtered, and evaporated under reduced pressure: yield 1.03 g (99%). analytical data are given in Table I.

Synthesis of Poly[bis(4-hydroxyphenoxy)phosphazene] (OHPOP, $[NP(OC_6H_4OH)_2]_n$ (7)) from Poly[bis(4-methoxyphenoxy)phosphazene] ($[NP(OC_6H_4OCH_3)_2]_n$ (3)). The procedure adopted for the preparation of this polymer is similar to that described for the synthesis of the corresponding trimer $[NP(OC_6H_4OH)_2]_3$, starting from 1.8 g (18.6 mmol) of BBr_3 in 30 mL of anhydrous CH_2Cl_2 and 2.1 g (7.2 mmol) of poly[bis(4-methoxyphenoxy)phosphazene]: yield 1.68 g (84.2%) of poly[bis(4-hydroxyphenoxy)phosphazene], which shows the characterization data reported in Table I; $M_w = 190\,000$; $T_g = +90$ °C.

Synthesis of Poly[bis(4-hydroxyphenoxy)phosphazene] (OHPOP, $[NP(OC_6H_4OH)_2]_n$ (7)) from Poly[bis(4-(benzyloxy)phenoxy)phosphazene] ($[NP(OC_6H_4OCH_2$-

$C_6H_5)_2]_n$ (4)). The preparation of the polymer 7 was carried out as above starting from 3.18 g (7.2×10^{-3} mol) of poly[bis(4-(benzyloxy)phenoxy)phosphazene] and 1.8 mL (1.86×10^{-2} mol) of BBr_3: yield 1.65 g (87%) of $[NP(OC_6H_4OH)_2]_n$ showing the characterization data reported in the previous example; M_w = 120 000.

Synthesis of Poly[bis(4-acetyloxy)phenoxy)phosphazene] ($[NP(OC_6H_4OCOCH_3)_2]_n$ (8)) by Acetylation of Poly[bis(4-hydroxyphenoxy)phosphazene] ($[NP(OC_6H_4OH)_2]_n$ (7)). A solution of 1.12 g (4×10^{-3} mol) of $[NP(OC_6H_4OH)_2]_n$ dissolved in 5 mL of dry pyridine was treated with 1.44 mL (1.5×10^{-2} mol) of acetic anhydride. After 2 h of stirring, the reaction mixture was poured into 50 mL of a 5% aqueous HCl solution. A white solid was collected, washed with water, filtered, and dried: yield 1.28 g (quantitative yield); analytical data are given in Table I.

Synthesis of Poly[bis(4-hydroxyphenoxy)$_{0.72}$(4-(benzyloxy)phenoxy)$_{1.28}$phosphazene] ($[NP(OC_6H_4OH)_{0.72}(OC_6H_4OCH_2C_6H_5)_{1.28}]_n$ (9)) from Poly[bis(4-(benzyloxy)phenoxy)phosphazene] ($[NP(OC_6H_4OCH_2C_6H_5)_2]_n$ (4)). The procedure for the synthesis of the copolymer 9 was similar to that reported above for the synthesis of hexakis(4-hydroxyphenoxy)cyclophosphazene from hexakis(4-benzyloxy)phenoxy)cyclophosphazene. In the present example, however, the following amounts of reagents were used: 0.5 g of carbon supporting 10% Pd; 2 g (4.5×10^{-3} mol) of $[NP(OC_6H_4OCH_2C_6H_5)_2]_n$ in 200 mL of THF and 20 mL of methanol; 2 atm of hydrogen pressure. The copolymer obtained was characterized by formation of the acetate derivative, as described in the following example.

Synthesis of Poly[bis(4-(acetyloxy)phenoxy)$_{0.72}$(4-(benzyloxy)phenoxy)$_{1.28}$phosphazene] ($[NP(OC_6H_4OCOCH_3)_{0.72}(OC_6H_4OCH_2C_6CH_5)_{1.28}]_n$ (10) from 9. The hydroxy phosphazene copolymer is acetylated by treatment with acetic anhydride according to the procedure described above for 6 and 8 starting from 0.3 g of $[NP(OC_6H_4OH)_{0.72}(OC_6H_4OCH_2C_6H_5)_{1.28}]_n$ in 2 mL of dry pyridine and 0.36 g of acetic anhydride. Yield 0.32 g (quantitative yield) of a product showing the following characterization data: Elemental anal.: C, 65.27; H, 4.93; N, 3.40 (corresponding to a phosphazene copolymer having the composition mentioned in the title); M_w = 450 000.

Results and Discussion

The synthetic strategy developed for introducing hydroxyl functions into phosphazene substrates involves preliminary exploratory work on low molecular weight cyclic trimers followed by extension of established synthetic procedures to the corresponding high molecular weight polymeric analogues.[17]

Model Reactions with Cyclic Trimers. In our work on cyclophosphazene model compounds we synthesized two different phosphonitrilic materials, i.e., hexakis(4-methoxyphenoxy)cyclophosphazene (MPT, $[NP(OC_6H_4OCH_3)_2]_3$ (1)) and hexakis(4-(benzyloxy)phenoxy)cyclophosphazene (BOPT) $[NP(OC_6H_4OCH_2C_6H_5)_2]_3$ (2)) by reaction of hexachlorocyclophosphazene with 4-methoxy- or 4-(benzyloxy)phenoxide, respectively, in boiling THF.

Both trimers were characterized by IR and NMR (^1H, ^{13}C, and ^{31}P) spectroscopy, and the corresponding data are reported in Table I.

^{31}P NMR spectra of these compounds show only sharp singlets around $\delta = +10$, indicating a complete and equivalent substitution of the chlorines in the parent hexachlorocyclophosphazene.

The different functional groups in the trimers are unequivocally identified by ^1H and ^{13}C NMR spectra. The methoxy group in the trimer 1 shows a singlet at $\delta = 2.10$ (^1H) and at $\delta = 55.80$ (^{13}C), while the CH_2 moiety of the benzyloxy substituent in the trimer 2 gives a singlet at $\delta = 4.73$ (^1H) and at $\delta = 70.70$ (^{13}C).

In the synthesized trimers 1 and 2 the hydroxyl functions are blocked by methyl and by benzyl residues, respectively. These groups can be removed by suitable deprotecting reactions according to Scheme II. As can be seen in Scheme II, methyl groups present in 1 are released by reaction with an excess of boron tribromide, while benzyl substituents in 2 are removed by a hydrogenation reaction under pressure in the presence of 10% palladium on carbon as a catalyst. According to McOmie,[15] the proposed reaction mechanism implies first the formation of a complex between BBr_3 and the oxygen of the methoxy group of 1, followed by the elimination of CH_3Br and the hydrolysis of the cyclophosphazene boron derivative. In the hydrogenation reaction of 2, on the contrary, the process of OH group formation takes place by release of the benzyl residue of the trimer as free toluene.[16]

In both cases a new trimer, i.e., hexakis(4-hydroxyphenoxy)cyclophosphazene (OHT, $[NP(OC_6H_4OH)_2]_3$), is formed which shows the analytical and characterization data reported in Table I for compound 5.

During these reactions, the phosphonitrilic ring system is preserved, as demonstrated by the presence in 5 of a sharp singlet at $\delta = +9.6$ in the ^{31}P NMR, by the permanence in the IR spectrum of the band located around 1250 cm^{-1} attributed to the asymmetric stretching of the $-P{=}N-$ group, and by the presence of peaks at 1170 and 945 cm^{-1} ascribed to the $P-O-C_6H_4$ vibrations.

It should be pointed out that a previous attempt to synthesize hexakis(4-hydroxyphenoxy)cyclophosphazene starting from hexakis(4-methoxyphenoxy)cyclophosphazene and HBr as deprotecting reagent gave only "a dark brown viscous oil", with no reported characterization data.[26]

High-Polymer Reactions. Following the above-described synthetic work on the cyclophosphazenes, the corresponding high molecular weight polymers, i.e., poly[bis(4-methoxyphenoxy)phosphazene] (3) and poly[bis(4-(benzyloxy)phenoxy)phosphazene] (4) were prepared by reaction of poly(dichlorophosphazene) [$(NPCl_2)_n$] with 4-methoxy- and 4-(benzyloxy)phenoxide, respectively, in boiling dioxane and in the presence of tetrabutylammonium bromide as phase-transfer catalyst.[27]

The obtained products are white, fibrous, film-forming polymers whose analytical characterization data are reported in Table I.

As in the case of the corresponding trimers, polymers 3 and 4 show sharp singlets located around $\delta = -17$ in the ^{31}P NMR spectra, indicating an almost complete substitution of the chlorines in the parent poly(dichlorophosphazene). Moreover, in the ^1H and ^{13}C NMR spectra of polymer 3 singlets are found at $\delta = 3.50$ (^1H) and $\delta = 55.40$ (^{13}C), which are attributed to the methoxy groups present in the side phenoxy substituents. In polymer 4, singlets are present at $\delta = 4.48$ (^1H) and $\delta = 70.01$ (^{13}C), assigned to the methylene moiety of the (benzyloxy)phenoxide.

The latent hydroxyl functions hidden in these POP are freed from the protective groups to produce poly[bis(4-hydroxyphenoxy)phosphazene] (OHPOP, $[NP(OC_6H_4OH)_2]_n$ (7)), following the same reaction sequence mentioned above for the corresponding trimers (Scheme II).

It should be pointed out, however, that both deprotection reactions, so satisfactorily used for the trimers, do not work equally well at polymeric level.

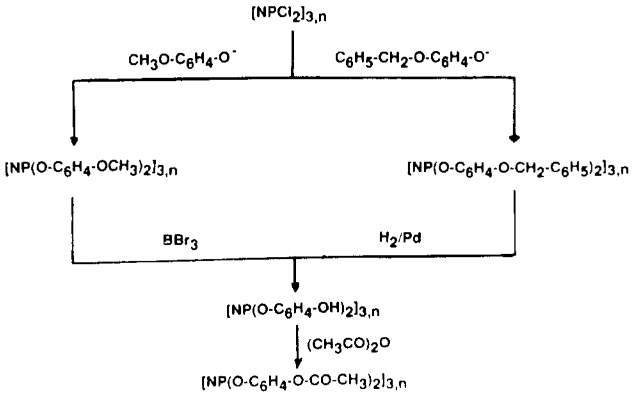
Let us examine these processes in more details.

(I) Reaction of Poly[bis(4-methoxyphenoxy)phosphazene] (3) or Poly[bis(4-(benzyloxy)phenoxy)phosphazene] (4) with BBr_3. As in the case of the above-reported trimer 1, reaction of BBr_3 with polymer 3 leads to the formation of 4-hydroxyphenoxy moieties on the phosphazene polymer, according to Scheme II. In the case of 3, however, a dramatic decrease of the weight-average

Table I
Characterization Data for Trimers and High Polymers

compd	elem anal.					^{31}P NMR, ppm	^{1}H NMR, ppm	^{13}C NMR, ppm	IR, cm^{-1}	mp, °C
		% C	% H	% N	% Cl					
1	calcd	57.73	4.81	4.81		+10.03	2.10 (s, 3 H, CH_3)	55.8 (q, CH_3)	1500	107–108
	found	57.45	4.90	4.70					1170	
							6.75 (4 H, aromatic AA′BB′ system)	114.9 (d, aromatic)	955	
								122.5 (d, aromatic)		
								157.4 (s, aromatic)		
2	calcd	70.43	4.96	3.16		+10.09	4.73 (s, 2 H, CH_2)	70.70 (t, CH_2)	1500	136
	found	70.49	5.00	2.67					1170	
							6.81 (4 H, aromatic AA′BB′ system)	115.90 (d, aromatic)	955	
								122.60 (d, aromatic)		
							7.35 (m, 5 H, aromatic)	128.10 (d, aromatic)		
								128.70 (d, aromatic)		
								129.20 (d, aromatic)		
								137.50 (s, aromatic)		
								145.20 (s, aromatic)		
								156.60 (s, aromatic)		
3	calcd	57.73	4.81	4.81	0	−17.56	3.50 (s, 3 H, CH_3)	55.40 (q, CH_3)	1500	
	found	56.49	4.72	4.35	0.5				1190	
							6.35 (m, 2 H, aromatic)	114.40 (d, aromatic)	950	
								122.80 (d, aromatic)	870	
							6.80 (m, 2 H, aromatic)	146.10 (s, aromatic)		
								156.00 (s, aromatic)		
4	calcd	70.43	4.96	3.16	0	−17.02	4.48 (s, 2 H, CH_2)	70.01 (t, CH_2)	1500	
	found	69.12	4.88	3.06	0.3				1190	
							6.60 (4 H, AA′BB′ system)	115.30 (d, aromatic)	950	
								123.00 (d, aromatic)	830	
							7.09 (s, 5 H, aromatic)	128.20 (d, aromatic)		
								128.30 (d, aromatic)		
								129.00 (d, aromatic)		
								137.80 (s, aromatic)		
								146.40 (s, aromatic)		
								156.00 (s, aromatic)		
5	calcd	54.76	3.80	5.32		+9.63	6.63 (s, CH, aromatic)	117.20 (d, CH, aromatic)	3250	241–243
	found	54.60	3.90	5.20				123.40 (d, CH, aromatic)	1600	
								145.10 (s, aromatic)	1500	
								156.40 (s, aromatic)	1250	
									1170	
									945	
6	calcd	55.35	4.03	4.03		+9.01	2.30 (s, 3 H, CH_3)	21.20 (q, CH_3)	1755	179
	found	54.79	4.02	3.80			6.95 (s, 4 H, aromatic)	122.50 (d, aromatic)	1495	
								123.30 (d, aromatic)	1160	
								148.50 (s, aromatic)	955	
								170.20 (s, C═O)		
7	calcd	54.76	3.80	5.32		−17.45	6.60 (4 H, aromatic AA′BB′ system)	116.80 (d, aromatic)	3250	
	found	50.73	3.72	5.09				123.90 (d, aromatic)	1510	
								146.50 (s, aromatic)	1190	
								154.90 (s, aromatic)	940	
									820	
8	calcd	55.35	4.03	4.03		−18.90	2.20 (s, 3 H, CH_3)	21.10 (q, CH_3)	1730	
	found	54.50	4.18	4.07			6.65 (m, 4 H)	122.3 (d, aromatic)	1495	
								122.8 (d, aromatic)	1370	
								147.70 (s, aromatic)	1180	
								149.40 (s, aromatic)	950	
								170.00 (s, C═O)		

Scheme II



molecular weight of the polymeric substrate (which collapses from the original value of 2 500 000 for **3** to 190 000 for **7**) was observed when 100% of the hydroxyl groups were formed. The same behavior was noted when poly[bis(4-(benzyloxy)phenoxy)phosphazene] (**4**) was treated with BBr_3 under comparable experimental conditions (final measured weight-average molecular weight was 120 000 starting from 2 500 000).

A possible explanation for this strong degradation can be put forward on the basis of the formation, together with the complex OCH_3/BBr_3, of a second acid–base adduct between BBr_3 and the nitrogen of the polyphosphazene skeleton (see Figure 1), which can induce chain scission of the polymer and degradation concurrently with a hydroxyl group deprotection reaction.

The existence of similar adducts between Lewis acids and cyclophosphazenes has been proved in the case of $AlBr_3/(NPCl_2)_3$,[28] $BCl_3/[NP(OCH_2CF_3)_2]_3$,[29,30] $BCl_3/(NPCl_2)_3$,[31] and $SO_3/[NP(OC_6H_5)_2]_3$[32] couples, while at the polymeric level they were found to be operative in the

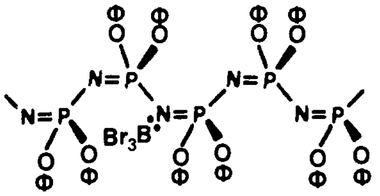


Figure 1. Acid–base adduct between BBr_3 and the polyphosphazene skeleton.

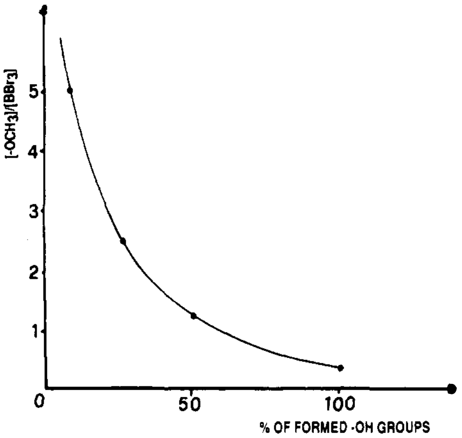


Figure 2. Percentage of free hydroxyl groups formed on the phosphazene polymer vs the $[OCH_3]/[BBr_3]$ ratio.

case of the sulfonation of poly(diphenoxyphosphazene) (PPP) with sulfur trioxide.[11] In the last case, moreover, an excess of SO_3 is needed to sulfonate the aromatic ring of the phenoxy moiety in the PPP, in close analogy to what was observed with the hydroxyl group deprotection process using BBr_3.

(II) Partial Deblocking of $[NP(OC_6H_4OCH_3)_2]_n$ (3) by Reaction with BBr_3. An attractive feature of the synthetic approach used to prepare free OH group containing polyphosphazenes is that the reaction of **3** with BBr_3 can be modulated to produce phosphazene copolymers containing variable percentages of hydroxyl functions. This can be achieved, for instance, by reacting the (methoxyphenoxy)phosphazene polymer with different amounts of BBr_3.

Figure 2 reports [polymer]/$[BBr_3]$ vs percentage of formed OH functions in the phosphazene material and shows that at $[OCH_3]/[Br] = 7.5$ only 7% of the methoxy functions are transformed into free hydroxyl groups, while a large excess of [Br] equivalents (100%) is needed to remove all the CH_3 protective groups of **3**.

The obtained phosphazene copolymers show, as expected, an increasing hydrophilic character at higher degrees of deblocking, and the 100% OH-containing polyphosphazene **7** was found to be soluble in dilute alkaline solutions.

It may be observed, moreover, that the demolition of the polyphosphazene skeleton is parallel to the deprotection process: the initial weight-average molecular weight ($M_w = 2\,500\,000$) of **3** decreases to 1 400 000 for the reaction in which only 7% of the methoxy protective functions are freed.

The above-mentioned possibility of introducing "a priori" controlled percentages of hydroxyl groups into selected phosphazene materials is an important fact in view of possible further functionalization reactions which may be carried out on these substrates.

(III) Hydrogenation Reaction of Poly[bis(4-(benzyloxy)phenoxy)phosphazene] (4). Preparative complications were also found when we tried to extend Pd-catalyzed hydrogenation reactions to poly[bis(4-(benzyloxy)phenoxy)phosphazene] (**4**) to synthesize the 100% OH group containing polymer **7**, in contrast to what was reported above for the formation of the hydroxylated trimer **5** from **2**.

Two main difficulties arose in this process. First, the deblocking of benzyl residues is a reaction which could never be driven to completeness, and only 50%, at the maximum, of the original (benzyloxy)phenoxy moieties could be successfully removed to form free hydroxyl functions. This occurred in spite of the numerous attempts carried out on polymer **4** using different experimental conditions (temperature, hydrogen pressure, percent catalyst, etc.). Second, the hydrogenation process was found to be highly irreproducible, and unpredictable percentages of OH groups were obtained in different experiments run under similar conditions. These facts seem to be related to poisoning phenomena in the Pd catalyst, probably due to the action of partially hydroxylated phosphazene copolymers formed in the process.

It may be pointed out, moreover, that also during the hydrogenation process of **4**, to produce partially hydroxylated phosphazene copolymers, chain breaking and degradation of the polyphosphazene substrate were observed; this is demonstrated by the measured value of the weight-average molecular weight (450 000) for acetylated copolymer (**10**), as compared to the initial value of 2 500 000 for polymer **4**.

Functionalization Reactions of 5 and 7. Hydroxyl group containing phosphazene materials **5** and **7** promise to be very versatile substrates due to the high reactivity of OH functions in a large variety of conditions.

Among the possible functionalizations which can be carried out to check the versatility of these substrates, the acetylation process seems to be very feasible, in view of the possible application of the acetylate trimer and polymers in photoresist technology.[33]

Toward this aim hexakis(4-hydroxyphenoxy)cyclophosphazene (**5**) and poly[bis(4-hydroxyphenoxy)phosphazene] (**7**) were dissolved in dry pyridine and treated with an excess of acetic anhydride, according to the reaction sequence described in Scheme II.

The obtained products **6** and **8** show sharp singlets at $\delta = +9.01$ and -18.90 in the ^{31}P NMR spectra, respectively, proving that both the inorganic ring and the chain are homogeneously substituted in this reaction. Moreover, the methyl group of the acetyl function in trimer **6** is identified by the singlets located at $\delta = 2.30$ (^1H) and $\delta = 21.20$ (^{13}C). Analogous evidence can be provided for polymer **8**, with singlets at $\delta = 2.20$ (^1H) and $\delta = 21.20$ (^{13}C).

Other chemical modifications of phosphazenes **5** and **7** carried out in our Institute are reported elsewhere.[18,19]

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References and Notes

(1) Sherrington, D. C.; Hodge, P., Eds. *Synthesis and Separations Using Functional Polymers*; Wiley: New York, 1988.

(2) Daly, H. W.; Lee, S.; Rungaroonthaikul, C. In *Chemical Reactions on Polymers*; Benham, J. L., Kinstle, Eds.; ACS Symposium Series 364; American Chemical Society: Washington, DC, 1988; Chapter 1, p 5.

(3) Frechet, J. M. J.; Farrall, M. J. In *Chemistry and Properties of Crosslinked Polymers*; Labana, S. S., Ed.; Academic Press: New York, 1977; p 59.

(4) Mathur, N. K.; Narang, C. K.; Williams, R. E. *Polymers as Aids in Organic Chemistry*; Academic Press: New York, 1980; p 18.

(5) Gleria, M. *Chim. Ind. (Milan)* **1988**, *70*, 15 (Supplement to *No. 11*).
(6) Allcock, H. R.; Kugel, R. L. *J. Am. Chem. Soc.* **1965**, *87*, 4216.
(7) Allcock, H. R.; Kugel, R. L.; Valan, K. J. *Inorg. Chem.* **1966**, *5*, 1709.
(8) Allcock, H. R. *Chem. Eng. News* **1985**, *63*, 22.
(9) Allcock, H. R. *Contemp. Top. Polym. Sci.* **1979**, *3*, 55.
(10) *Functional Monomers and Polymers. Procedures, Synthesis, Applications*; Takemoto, K., Inaki, Y., Ottembrite, R. M., Eds.; Marcel Dekker: New York, 1987.
(11) Montoneri, E.; Gleria, M.; Ricca, G.; Pappalardo, G. C. *Makromol. Chem.* **1989**, *190*, 191.
(12) Gleria, M.; Bolognesi, A.; Porzio, W.; Catellani, M.; Destri, S.; Audisio, G. *Macromolecules* **1987**, *20*, 469.
(13) For example, see: Gleria, M.; Lora, S.; Minto, F.; Busulini, L.; Paolucci, G. *Chim. Ind. (Milan)* **1981**, *63*, 719.
(14) For example, see: Allcock, H. R.; Kwon, S. *Macromolecules* **1989**, *22*, 75.
(15) McOmie, J. F. W.; Watts, M. L.; West, D. E. *Tetrahedron* **1968**, *24*, 2289.
(16) Heathcock, C. H.; Ratcliffe, R. *J. Am. Chem. Soc.* **1971**, *93*, 1746.
(17) Allcock, H. R. *Acc. Chem. Res.* **1979**, *12*, 351.
(18) Medici, A.; Fantin, G.; Pedrini, P.; Gleria, M.; Facchin, G. Italian Patent 000462 MI A/91.
(19) Gleria, M.; Medici, A.; Fantin, G.; Fogagnolo, M., Bertani, R. Italian Patent 000916 MI A/91.
(20) For example, see: Gleria, M.; Minto, F.; Lora, S.; Busulini, L.; Bortolus, P. *Macromolecules* **1986**, *19*, 574.
(21) Vogel, A. J. *A Textbook of Practical Organic Chemistry*; Longmans: London, 1970.
(22) Allcock, H. R. *Phosphorus–Nitrogen Compounds*; Academic Press: New York, 1972.
(23) Reference 22, p 429.
(24) Singler, R. E.; Hagnauer, G. L.; Schneider, N. S.; LaLiberte, B. R.; Sacher, R. E.; Matton, R. W. *J. Polym. Sci., Polym. Chem. Ed.* **1974**, *12*, 433.
(25) Quinn, E. J.; Dieck, R. L. *J. Fire Flammability* **1976**, *7*, 5.
(26) Kober, E. H.; Lederle, H. F.; Ottmann, G. F. U.S. Patent 3,462,518, 1969.
(27) Austin, P. E.; Riding, G. H.; Allcock, H. R. *Macromolecules* **1983**, *16*, 719.
(28) Coxon, G. E.; Sowerby, D. B. *J. Chem. Soc. London, A* **1969**, 3012.
(29) Horn, H. G.; Kolkmann, F. *Makromol. Chem.* **1982**, *183*, 1833.
(30) Horn, H. G.; Kolkmann, F. *Makromol. Chem.* **1982**, *183*, 1843.
(31) Sennett, M. S.; Hagnauer, G. L.; Singler, R. E.; Davies, G. *Macromolecules* **1986**, *19*, 959.
(32) Montoneri, E.; Ricca, G.; Gleria, M.; Gallazzi, M. C. *Inorg. Chem.* **1991**, *30*, 150.
(33) Tessier, T. G.; Frechet, J. M. J.; Willson, C. G.; Ito, H. In *Materials for Microlithography*; Thompson, L. F., Willson, C. G., Frechet, J. M. J., Eds.; ACS Symposium Series 266; American Chemical Society: Washington, DC, 1984; Chapter 13, p 269.

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