Functionalization of Poly[(alkoxy)phosphazenes]: Synthesis and Characterization of Poly(phosphazenes) Containing Hydroxyl Groups

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ABSTRACT: Methoxy end groups were cleaved from poly[bis(methoxyalkoxy)phosphazenes] $\{NP[(OCH_2CH_2)_mOCH_3]_2\}_n$, where $m = 2$ (**2**, MEEP) and $m = 1$ (**3**, MEP) by reaction with trimethylsilyl iodide to give silylated polymers $\{NP[(OCH_2CH_2)_mOSiMe_3]_x\ [(OCH_2CH_2)_mOCH_3]_y\}_n$ ($x + y = 2$; $m = 2$ (**4**), $m = 1$ (**5**)). The silylated polymers **4** and **5** were hydrolyzed in a second step to yield the alcohol-functionalized polymers $\{NP[(OCH_2CH_2)_mOH]_x\ [(OCH_2CH_2)_mOCH_3]_y\}_n$ ($m = 2$ (**6**), $m = 1$ (**7**)). The structures of both classes of compounds were investigated by ^{31}P, ^{13}C, and ^1H NMR and infrared spectroscopies. The correlation between the amount of $ISiMe_3$ and the percentage of resultant alcohol functions was established. This latter was estimated by first using ^1H NMR and secondly ^{31}P NMR. In the latter case use was made of the reaction of a bicyclophosphane **8** with the OH groups in **6** and **7**, which leads to bicyclophosphorane-functionalized polymers. The two results are in agreement. The presence of the alcohol function was confirmed by the observation of cross-linking through the reactions of **6** and **7** with a diisocyanate and a polyphosphazene functionalized by succinic anhydride groups. This functionalization reaction induces chain degradation of the polymer as the percentage of alcohol functions increases.

Introduction

At the present time, research in macromolecular chemistry is moving more and more toward the formation of high technological materials, and the chemical modification of known macromolecules could be the means to obtain new structures at lower cost.

In this area, poly(phosphazenes) are of great interest, since from the same precursor, poly(dichlorophosphazene), $[NPCl_2]_n$ or PCPZ (**1**) (first disclosed by Allcock and co-workers[1] in 1965), we can obtain a large variety of products with versatile properties. Indeed, the extreme reactivity of chlorine atoms in PCPZ toward nucleophiles can be used to bind a large variety of substituents to the phosphazene chain and the great number of structures so obtained obviously give rise to diverse physical and chemical properties. The polymers can be hydrophobic or hydrosoluble, electrical conductors or insulators, photodegradable or photoresistant, and resistant or not to solvents. Furthermore they are often self-extinguishing and have T_g values between −100 and +100 °C.[2–6]

The first route to obtain polymers with predictable properties consists naturally of the use of suitable substituents. The second can be the use of multicomponent blends, containing poly[(organo)phosphazene] (POPZ) and other components, macromolecular or not. Nevertheless, in this case, the synthesis of suitable functionalized poly(phosphazenes) becomes important.

A great variety of functional groups can be introduced onto poly(phosphazenes)—firstly, by direct nucleophilic substitution or cosubstitution of **1**,[7] secondly, by chemical modification of groups attached to the phosphorus by the first method,[8,9] thirdly, directly by condensation polymerization,[10,11] and lastly, by modification of alkyl and aryl groups on polyphosphazenes formed by the third method.[12]

A very interesting and reactive function to introduce is the alcoholic function because beyond the particular properties it gives to the polymers, it also allows almost all the reactions of OH groups directly on the polymer that extend the number of potential applications. This property is particularly important in the coating field or for the production of adhesives for which low cross-linking temperatures are often required.

In this area, little has been reported. However some functionalized poly(phosphazenes) have been synthesized bearing primary, secondary, and tertiary[13,14] alcohol groups. In any case, they are obtained using a chemical modification of substituents in POPZ polymers. These syntheses can be done using protecting and deprotecting reactions of the OH functions before and after the substitution of PCPZ.[9,15–19] Nevertheless it seems more interesting to avoid the preliminary protecting reaction and directly functionalize already-known POPZ.

This work describes the formation of alcohol-functionalized polymers from poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene] (**2**) and poly[bis(2-methoxyethoxy)phosphazene] (**3**) (respectively named MEEP and MEP).

We will detail successively the functionalization process, the characterization of the polymers, the evaluation of the percentage of OH groups formed, and

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Table 1. Spectroscopic Characterization Data for 4−7

	4	**5**	**6**	**7**
^{31}P NMR δ, ppm	−6	−6	<6 < δ < −5.6	−6 < δ < −3.4
^{13}C NMR δ, ppm	72.9 ($\mathit{C}H_2CH_2OSiMe_3$ 72.4 ($POCH_2\mathit{C}H_2$) 70.8 ($\mathit{C}H_2\mathit{C}H_2OCH_3$) 65.5 ($PO\mathit{C}H_2$) 62.3 ($CH_2\mathit{C}H_2OSiMe_3$) 59.3 ($O(\mathit{C}H_3)_3$) 0.09 ($OSi(\mathit{C}H_3)_3$)	72.3 ($\mathit{C}H_2OCH_3$) 67.1 ($\mathit{C}H_2OSiMe_3$) 65.4 ($PO\mathit{C}H_2CH_2OCH_3$) 62.4 ($PO\mathit{C}H_2CH_2OSiMe_3$) 59.1 ($O\mathit{C}H_3$) 0.1 ($OSi(\mathit{C}H_3)_3$)	73.2 ($\mathit{C}H_2CH_2OH$) 72.5 ($POCH_2\mathit{C}H_2$) 70.8 ($\mathit{C}H_2\mathit{C}H_2OCH_3$) 65.7 ($PO\mathit{C}H_2$) 62.0 ($CH_2\mathit{C}H_2OH$) 59.3 ($O\mathit{C}H_3$)	72.2 ($\mathit{C}H_2OCH_3$) 68.7 ($\mathit{C}H_2OH$) 65.7 ($PO\mathit{C}H_2CH_2OCH_3$) 62.3 ($PO\mathit{C}H_2CH_2OH$) 59.1 ($O\mathit{C}H_3$)
^{1}H NMR δ, ppm	4.03 ($POC\mathit{H}_2$) 3.66 3.60 ($POCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2$) 3.49 3.33 ($OC\mathit{H}_3$) 0.10 ($OSi(C\mathit{H}_3)_3$)	4.05 ($POC\mathit{H}_2CH_2OCH_3$) 3.95 ($POC\mathit{H}_2CH_2OSiMe_3$) 3.69 ($C\mathit{H}_2OSiMe_3$) 3.53 ($C\mathit{H}_2OCH_3$) 3.32 ($OC\mathit{H}_3$) 0.08 ($OSi(C\mathit{H}_3)_3$)	4.05 ($POC\mathit{H}_2$) 3.61 3.55 ($POCH_2C\mathit{H}_2OC\mathit{H}_2C\mathit{H}_2$) 3.48 3.32 ($OC\mathit{H}_3$)	4.05 ($POC\mathit{H}_2$) 3.69 ($C\mathit{H}_2OH$) 3.53 ($C\mathit{H}_2OCH_3$) 3.32 ($OC\mathit{H}_3$)
IR, cm^{-1}	1239 (δ_{CH_3}) 842, 758 (ν_{SiCH_3})	1240 (δ_{CH_3}) 839, 740 (ν_{SiCH_3})	3400 (ν_{O-H})	3403 (ν_{O-H})

finally, the cross-linking reactions that we have performed.

Results and Discussion

Overal Synthetic Approach. The functionalization process is based on the reaction of trimethylsilyl iodide (Me_3SiI) with ethers[20-22] according to (1).

$$\begin{gathered}R{-}O{-}R' + ISi(CH_3)_3 \xrightarrow{-R'I} R{-}O{-}Si(CH_3)_3 \xrightarrow{H_2O} \\ ROH + (CH_3)_3SiOH \xrightarrow{-H_2O} (Me_3Si)_2O \quad (1)\end{gathered}$$

The selectivity of this reaction allowed us to consider its application to the methoxy groups containing POPZ (**2** and **3**) in order to obtain alcohol functions according to (2).

$$\begin{gathered}[NP((OCH_2CH_2)_mOCH_3)_2]_n \xrightarrow[-CH_3I]{+Me_3SiI} \\ m = 2\ (\mathbf{2}),\ m = 1\ (\mathbf{3}) \\ [NP((OCH_2CH_2)_mOSiMe_3)_x((OCH_2CH_2)_mOCH_3)_{2-x}]_n \\ m = 2\ (\mathbf{4}),\quad m = 1\ (\mathbf{5}) \\ \xrightarrow[-(Me_3Si)_2O]{+H_2O} [NP((OCH_2CH_2)_mOH)_x((OCH_2CH_2)_mOCH_3)_{2-x}]_n \\ m = 2\ (\mathbf{6}),\ m = 1\ (\mathbf{7}) \\ (2)\end{gathered}$$

For that, **1** was previously obtained by polycondensation of *P,P,P*-trichloro-*N*-(dichlorophosphoryl)monophosphazene,[23,24] $Cl_3P{=}NP(O)Cl_2$. **2** and **3** were thereafter synthesized by reaction of **1** with suitable alcoholates,[25] treated with various amounts of Me_3SiI (from 10 to 50 molar % with respect to the substituents[26]) and finally hydrolyzed.

The intermediate silylated polymers **4** and **5** and the final hydroxylated polymers **6** and **7** were all characterized by ^{1}H, ^{31}P, and ^{13}C NMR and infrared spectroscopies. A summary of these data is presented in Table 1.

^{1}H NMR. The formation of **4** from **2** is characterized by the appearance of a signal around $\delta = 0.1$ ppm ($OSiCH_3$) for which the intensity grows with the increase in Me_3SiI and the simultaneous decrease of the signal at $\delta = 3.3$ ppm (OCH_3) (Figure 1). This result confirms the first step of the reaction (2). The second step, that consists of the hydrolysis reaction of **4** to give **6**, is distinguished by the almost complete disappearance of the signal at $\delta = 0.1$ ppm without any other real modification of the ^{1}H NMR spectrum of **4**. (The small signal around $\delta = 0.1$ ppm can be attributed to some residual $(Me_3Si)_2O$.)

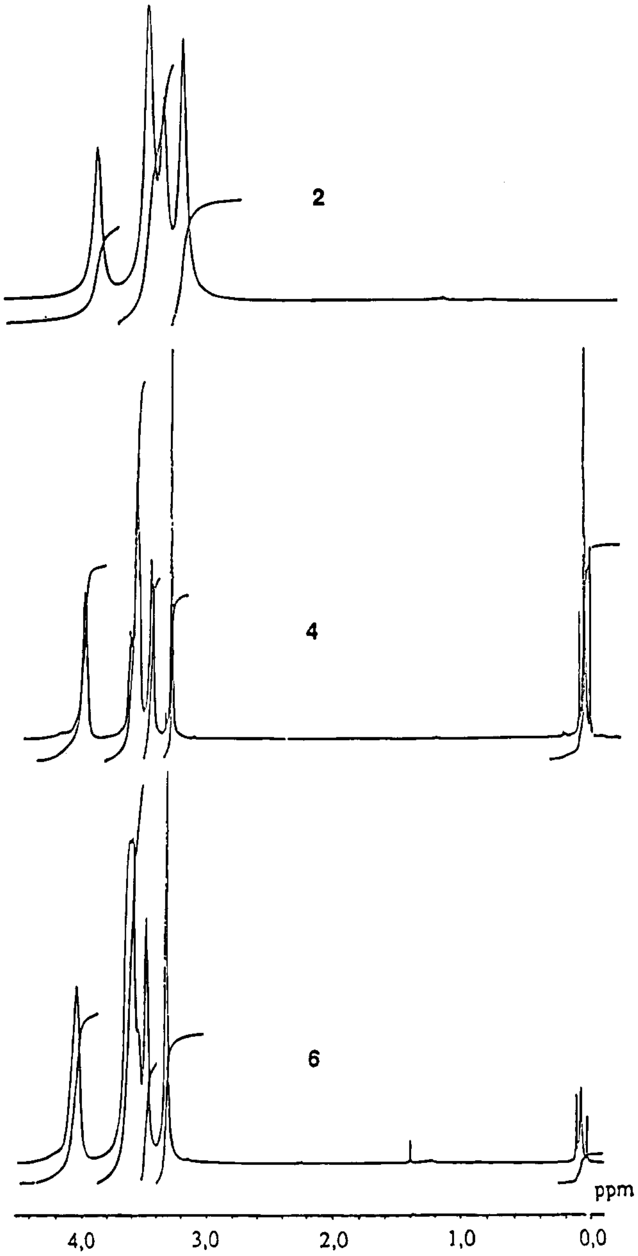


Figure 1. ^{1}H NMR spectra of polymers **2**, **4**, and **6**.

In the case of the polymers **3**, **5**, and **7**, we observe the same evolutions of the signals at $\delta = 3.3$ ppm and $\delta = 0.1$ ppm. But in addition the change from **3** to **5** is characterized by the splitting into two signals of the one

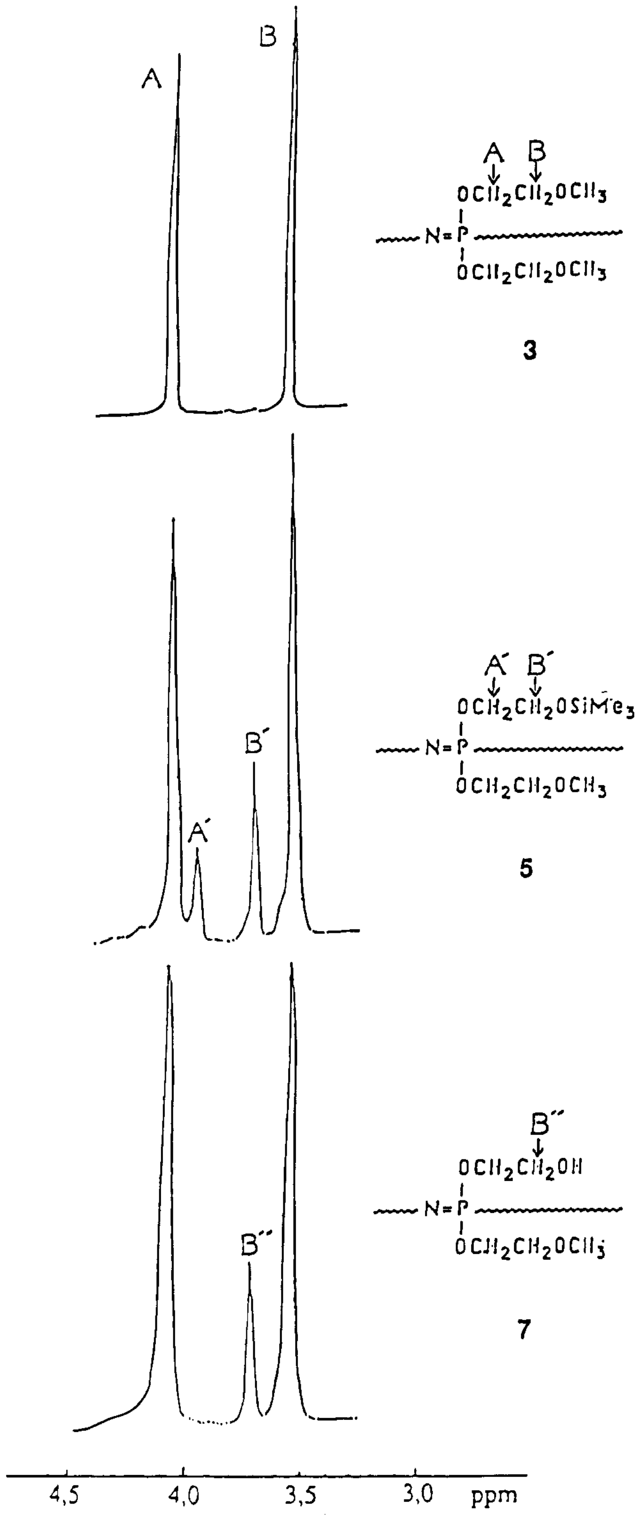


Figure 2. ${}^1H$ NMR spectra (from $\delta = 3.4$ to 4.1 ppm) of polymers **3**, **5**, and **7**.

(A) assigned to $POCH_2$ in **3** (Figure 2). In fact a new signal (A′) at $\delta = 3.95$ ppm appears, whose intensity grows with the increase in Me_3SiI and balances the decrease of the intensity of signal A. A′ and A are assigned to $POCH_2CH_2OSiMe_3$ and $POCH_2CH_2OCH_3$, respectively. A similar comment can be made for the signals at $\delta = 3.7$ ppm (B′) and $\delta = 3.5$ ppm (B) assigned to CH_2OSiMe_3 and CH_2OCH_3, respectively. The signals representative of the $POCH_2$ protons in **7** are both at $\delta = 4.05$ ppm.

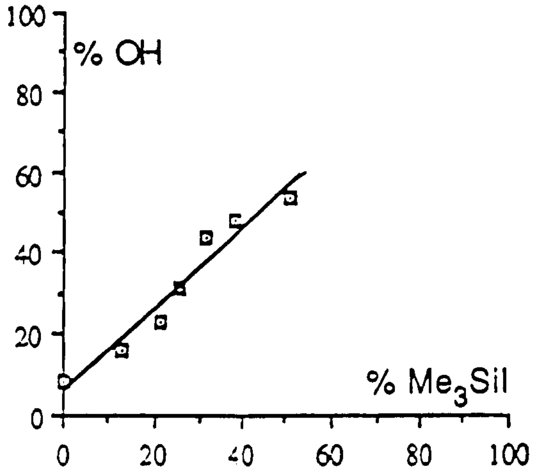
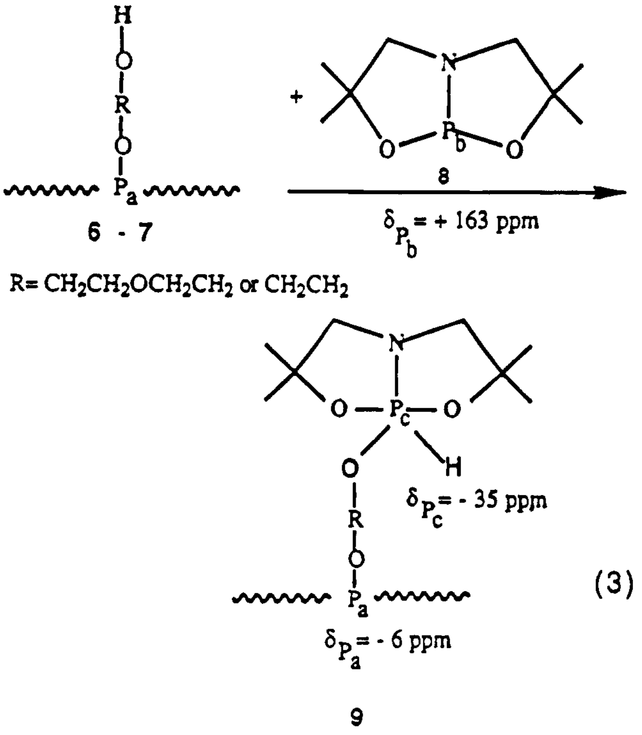


Figure 3. Variations of % OH groups versus % Me_3SiI (${}^1H$ NMR) for polymers **6**.

Determination of the Percentage of Grafted OH Groups. By the quantitative study of the ${}^1H$ NMR, it is possible not only to follow the evolution of the reaction but also to deduce the percentage of OH functions introduced. As an example, it can be obtained from the ratio of the OCH_3 protons ($\delta = 3.3$ ppm) to the $PO\mathbf{CH_2}$ ($\delta = 4.05$ ppm) protons. This has been done for polymers **6** and **7**.

The variations of the percentage of OH functions as a function of the percentage of Me_3SiI introduced are represented in Figure 3 in the case of polymers **6**.[27] The correlation is good. The yield in the cleavage reaction of methoxy groups is close to 100%.

${}^{31}P$ NMR. It was possible to confirm the former results by using the reaction of 3,3,7,7-tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane (**8**) with hydroxylic functions. This bicyclophosphane **8** reacts differently depending on whether the OH groups come from alcohol or from water.[28] In ${}^{31}P$ NMR, the phosphorus atoms of the reaction products then have different chemical shifts ($\delta = -35$ ppm after reaction with alcohols, **8a**; $\delta = +18$ ppm, **8b**, and $\delta = -7$ ppm **8c**, after reaction with water[29]) (Scheme 1). In our case, polymer **6** or **7** reacts with **8** giving **9** according to (**3**).



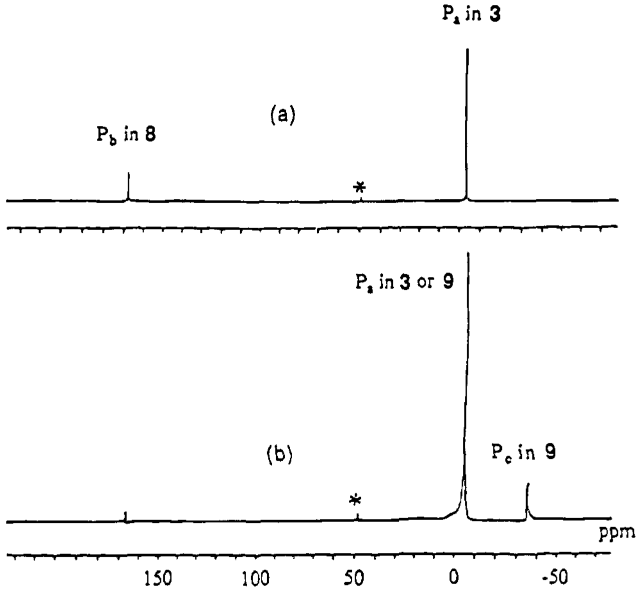


Figure 4. ^{31}P NMR spectra of polymers **3** (a) and **7** (b) after addition of **8**. The asterisk denotes a nonidentified impurity of **8**.

After reaction of an excess of **8** with **6** or **7**, the ratio of the intensities of the P_a and P_c signals allows the percentage of OH functions to be determined (Figure 4).

The results obtained (referring to the Experimental Section) are in accordance with those deduced from ^1H NMR spectra (Figure 5).

Properties of the Polymers. All the polymers are viscous brown oils at room temperature. Intermediate silylated polymers **4** and **5** are soluble in chloroform, tetrahydrofuran, and benzene. Hydroxylated polymers **6** and **7** are soluble in chloroform, dimethylformamide, and water, but insoluble in tetrahydrofuran. Nevertheless this functionalization reaction, like others,[9] induces chain degradation of the polymer, as the intrinsic viscosity measurements show. For instance, in the case of polymer **6**, the viscosity decreases from $[\eta] = 52$ mL/g for the starting polymer **2** to $[\eta] = 36$ mL/g for a 50% hydroxylated polymer. In the case of **7**, the variation is of the same order of magnitude.

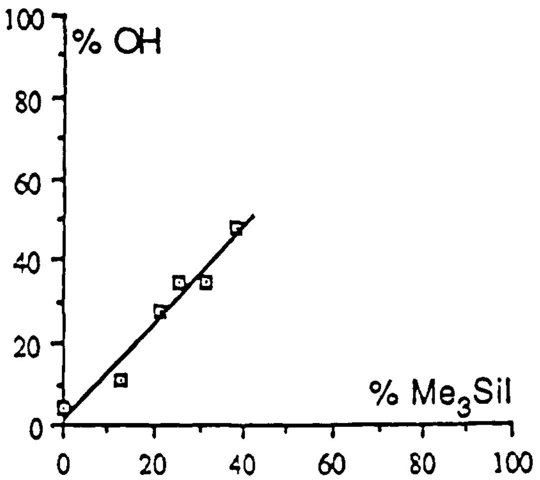


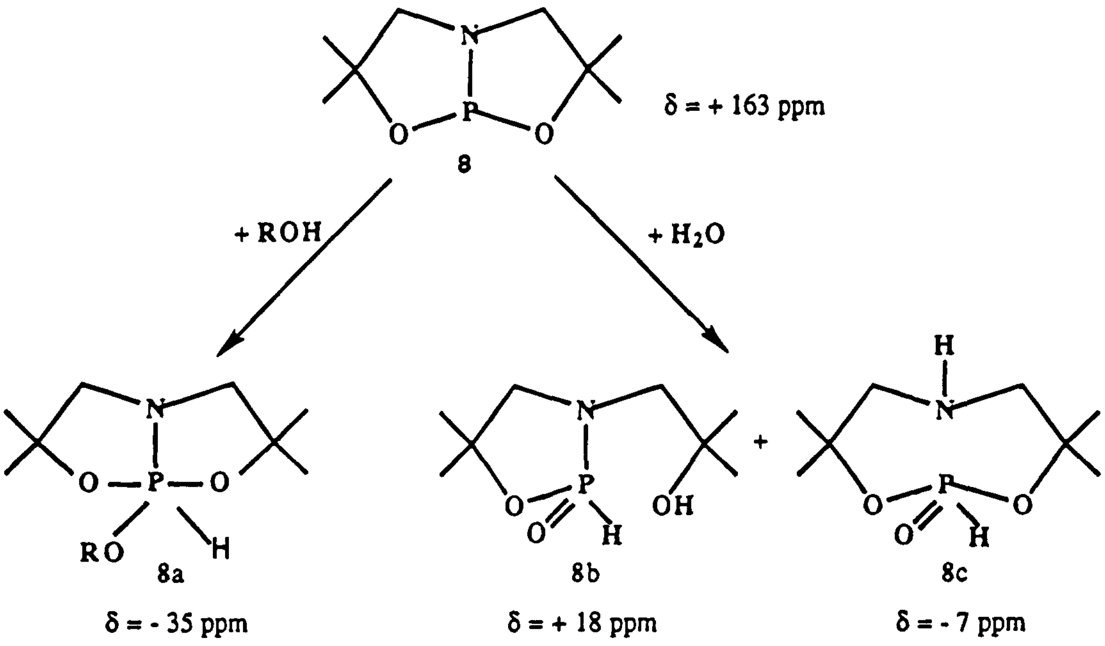
Figure 5. Variations of % OH groups versus % Me_3SiI (^{31}P NMR) for polymers **6**.

This degradation does not occur in the case of P–C bonds containing polyphosphazenes such as poly(methylphenylphosphazenes) which are synthesized by deprotonation/substitution reaction of the *P*-methyl groups.[14]

Infrared Spectroscopy. The presence of silylated groups in **4** or **5** is characterized by three absorption bands at $\nu = 1239$, 842, and 758 cm^{-1} in the first case and at 1240, 839, and 740 cm^{-1} in the second, whose intensities grow with the increase in Me_3SiI. These bands are characteristic of the $\delta(CH_3)$ and $\nu(Si-CH_3)$ vibrations in $-Si(CH_3)_3$. The conversion of **4** to **6** or **5** to **7** is distinguished by the appearance of a broad band around $\nu = 3400$ cm^{-1} ($\nu(OH)$). Figure 6 shows the increase in intensity of this band with the percentage of hydroxyl groups.

Cross-Linking Reactions of Polymers 6 and 7. The introduction of OH functions along the polymer chain is interesting, as it gives rise to reaction sites. Therefore, we checked the reactivity of the OH groups with diisocyanate and anhydride functions which according to (4) and (5) must lead to the cross-linking of **6** and **7**.

Scheme 1



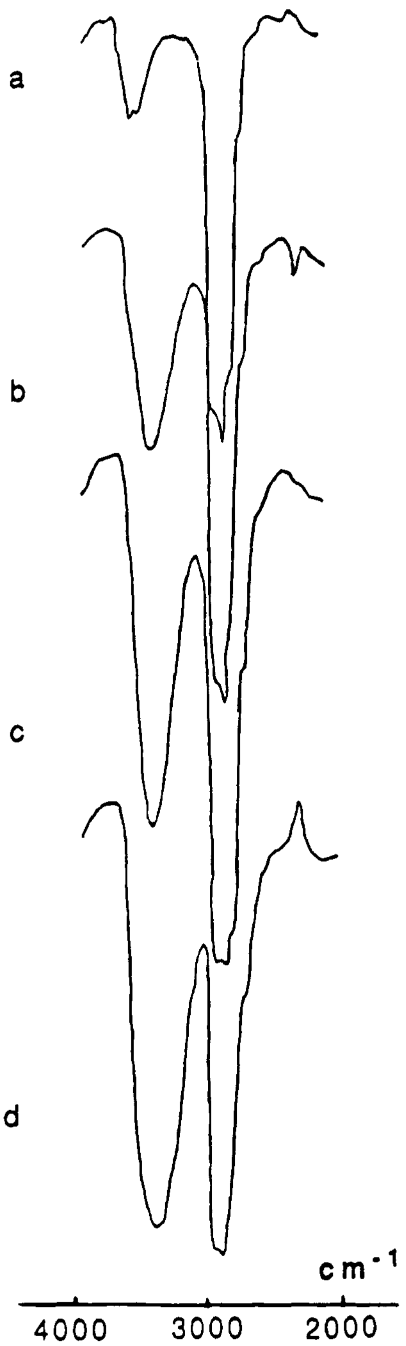
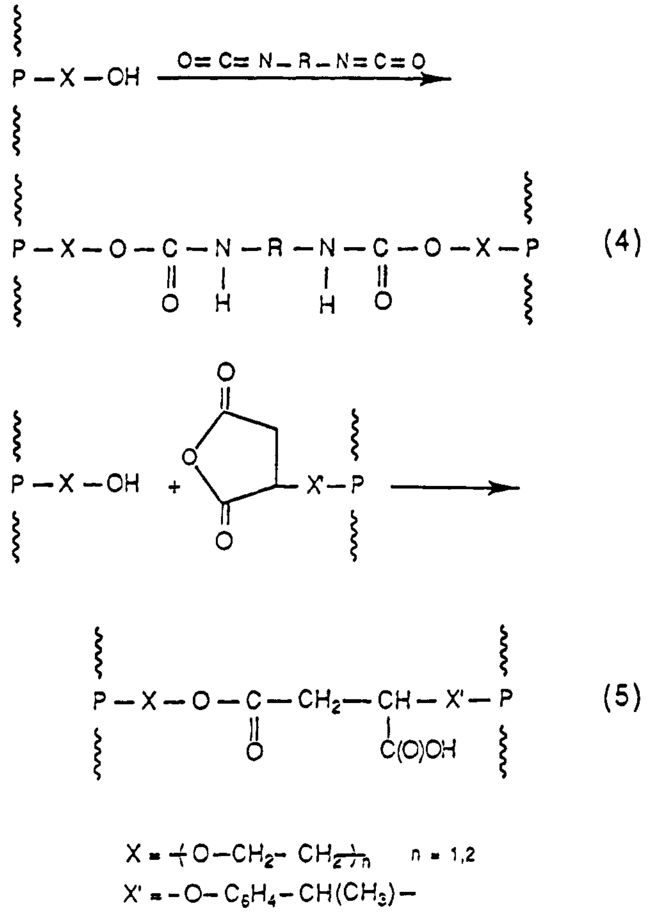


Figure 6. Infrared spectra of MEEP **3** (a) and polymers **6** with the increasing number of hydroxylic groups (b–d).

Reaction of a Diisocyanate with 6 and 7. The reactions of **6** and **7** with hexamethylene diisocyanate (HDI), under conditions similar to those of Allcock and co-workers,[16] give insoluble gels after 1–7 days at room temperature depending on the concentration of the OH functions. After washing with water, the gels yield infrared spectra with bands characteristic of polyphosphazenes.

Reaction of 6 and 7 with an Anhydride. The reaction of **6** with a poly[(phenoxy-, *p*-ethylphenoxy)-phosphazene], functionalized by succinic anhydride groups according to Gleria and co-workers,[30] also gives insoluble gels at room temperature at the end of several days. After washing and drying, the gels have infrared spectra with a band at $\nu = 1735$ cm^{-1} characteristic of ester functions which have been formed.

It is clear that the partial and controlled introduction of alcohol groups in poly[bis(alkoxy)phosphazenes] using trimethylsilyl iodide is a versatile and easy to use process. It can offer interesting perspectives for the applications of phosphazene materials as polymer–metal, polymer–glass, and polymer–polymer adhesives or coatings. It could be possible to make use of this process for the functionalization of suitable structures containing only a minimum number of etheric side groups.



Experimental Section

Materials. Most experimental manipulations were performed under an atmosphere of dry nitrogen. Tetrahydrofuran, chloroform, dimethylformamide, and *n*-heptane were obtained from SDS; 2-methoxyethanol and 2-(2-methoxyethoxy)ethanol, from Carlo Erba. These materials (analytical grade) were used after drying on molecular sieves. Sodium was washed with dry petroleum ether before use. Hexamethylenediisocyanate, 2,4-bis(dimethylamino)pyridine, and iodotrimethylsilane were Aldrich products (analytical grade) and used as received. Poly(dichlorophosphazene) (**1**) was prepared by thermal polycondensation of $Cl_3PNP(O)Cl_2$ as described previously.[23,24]

Equipment. NMR spectra were recorded in $CHCl_3$ (^{31}P and ^{13}C) or $CDCl_3$ (^1H) solutions using a Bruker WP 80 or a Bruker WP 400 NMR spectrometer, respectively. Chemical shifts are relative to external 85% H_3PO_4 (^{31}P) or external TMS (^1H, ^{13}C). FTIR spectra were recorded with a Perkin-Elmer spectrometer (model M.1720) from films between KBr windows. Viscosimetry measurements were made on $CHCl_3$ solutions at 30 °C using an automatized AVS Schott viscosimeter.

Synthesis of 3,3,7,7-Tetramethyl-2,8-dioxa-5-aza-1-phosphabicyclo[3.3.0]octane (8). **8** was obtained by the reaction of 1,1,5,5-tetramethyl-3-aza-1,5-pentanediol, $HOC(CH_3)_2CH_2NHCH_2C(CH_3)_2OH$, with tris(dimethylamino)phos-

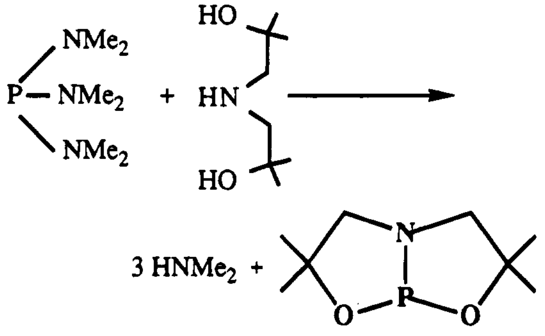
Table 2

amt of polymer **2**, mol × 10^2	amt of $ISi(CH_3)_3$, mol × 10^2	amt of H_2O, mol × 10^2	x in **6**[a]	x in **9**[b]
1	0.26	1.18	0.32	0.22
1	0.43	2.0	0.46	0.56
1	0.51	2.37	0.62	0.70
1	0.63	1.58	0.87	0.70
1	0.76	2.18	0.96	0.96

amt of polymer **3**, mol × 10^2	amt of $ISi(CH_3)_3$, mol × 10^2	amt of H_2O, mol × 10^2	x in **7**[a]	x in **9**[b]
1	0.21	1.07	0.21	0.18
1	0.42	2.13	0.32	
1	0.48	2.41	0.54	0.36
1	0.69	3.46	0.78	0.92
1	1.11	4.82	1.04	1.18

[a] Experimental values of x for polymers **6**[27] and **7** determined by ^1H NMR. [b] Experimental values of x for polymers **9** determined by ^{31}P NMR.

phane, $P(NMe_2)_3$, according to (6) and following the experimental procedure described previously.[31]



(6)

8

Synthesis of Poly[bis(2-(2-methoxyethoxy)ethoxy)phosphazene], MEEP (2), and Poly[bis(2-methoxyethoxy)phosphazene], MEP (3). **2** and **3** were prepared as reported elsewhere.[25] After synthesis, these polymers were purified by precipitation from THF into *n*-heptane (2×) and by dialysis against water for 8 days. The products were thoroughly dried under vaccum (0.1 Torr) and by passing a $CHCl_3$ solution over molecular sieves (yield 70% for **2** and 85% for **3**).

A ^{31}P NMR spectrum consisted of a sharp singlet at $\delta = -6.2$ ppm, which was indicative of a total halogen replacement.

General Synthetic Route to Silylated and Hydroxylated Polymers 4–7. $ISiMe_3$ was slowly added to a solution of **2** or **3** in $CHCl_3$ at room temperature. The mixture was warmed to 30–35 °C and stirred during 3 days. The solvent was then removed under vacuum (0.1 Torr) to give **4** and **5**. Next, solutions of **4** or **5** in THF were hydrolyzed by water at ambient temperature during 1 h to give solutions of **6** and **7**. After drying by passing over molecular sieves, THF was removed under vacuum (0.1 Torr).

The yield of the silylation–hydrolysis reactions was about 90%.

A group of stoichiometries and values for X in **6**, **7**, and **9** is given in Table 2.

Synthesis of Poly[(phenoxy-, ethylphenoxy)phosphazene] Functionalized by Succinic Anhydride Groups. Poly[(phenoxy-, *p*-ethylphenoxy)phosphazene] functionalized by succinic anhydride groups was prepared as reported elsewhere.[30] To a solution of poly[(phenoxy-, ethylphenoxy)phosphazene] (5 g) in xylene (100 mL) at room temperature, were slowly added 3 g of maleic anhydride and 0.5 g of benzoyl peroxide. The mixture was warmed to 125 °C and stirred during 20 min. The polymer was then precipitated into methanol at −5 °C.

Evaluation of the Hydroxylic Functions Content of 6 and 7 by ^{31}P NMR. For this determination, a concentrated solution of bicyclophosphane **8** in $CHCl_3$ was added directly in the NMR tubes containing the $CHCl_3$ solutions of polymers **6** or **7**.

Cross-Linking Reactions of Polymer 6 or 7 with Hexamethylene Diisocyanate. Hexamethylene diisocyanate (60 μL) was added quickly to **6** or **7** (1 g) and 2,4-bis(dimethylamino)pyridine (60 μg) dissolved in dry DMF (6–7 g). After homogenization by stirring, the solution began to gel at room temperature after 1–7 days depending on the hydroxylic function content of the polymers.

Cross-Linking Reactions of Polymers 6 with Poly[(phenoxy-, *p*-ethylphenoxy)phosphazene] Functionalized by Succinic Anhydride Groups. A 1 mL aliquot of a solution of **6** (10% in CH_2Cl_2) was mixed with 1 mL of a solution of poly[(phenoxy-, ethylphenoxy)phosphazene], functionalized by succinic anhydride groups (10% in CH_2Cl_2). The solution began to gel after 24 h at room temperature. Seven days later, it was totally gelled.

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