The Reaction of Poly(chlorophosphazene)s with *p*-Aminophenol − Specific Formation of Aminophosphazenes with Terminal OH Groups and Aryloxyphosphazenes with Terminal NH_2 Groups

Gabino A. Carriedo,*[a] José. I. Fidalgo Martínez,[a] F. J. García Alonso,[a] E. Rodicio González,[a] and A. Presa Soto[a]

Keywords: Polymers / Inorganic polymers / Polyphosphazenes / *p*-Aminophenol

The outcome of the reaction of the bifunctional reagent *p*-aminophenol (HO-C_6H_4-NH_2) with the cyclic triphosphazene [$N_3P_3Cl_6$] is very dependent on the solvent, the temperature, and the proton abstractor. In THF at room temperature with K_2CO_3 the reaction is very slow and takes place only through the NH_2 group to give a mixture of aminophosphazenes, but in refluxing acetone with Cs_2CO_3 the reaction is fast and occurs through both the NH_2 and the OH groups leading to crosslinked products. The analogous reaction with the bis-spirocyclodichlorotriphosphazene [$N_3P_3Cl_2(O_2C_{12}H_8)_2$] ($O_2C_{12}H_8$ = 2,2′-dioxybiphenyl) is also dependent on the conditions, but is more selective. At room temperature in THF with K_2CO_3 the reaction gives mostly aminophosphazene derivatives, while in refluxing acetone with Cs_2CO_3 the known aryloxyphosphazene [$N_3P_3(OC_6H_4NH_2)_2(O_2C_{12}H_8)_2$] (**1**) is obtained exclusively. Accordingly, the reactions of *p*-aminophenol with high molecular weight poly(dichlorophosphazene) $[NPCl_2]_n$ in THF at room temperature in the presence of K_2CO_3, occur exclusively through the NH_2 groups without crosslinking, forming solutions of the aminophosphazene random copolymers $\{[NPCl_2]_{1-x}[NPCl(NHC_6H_4OH)]_x\}_n$ (**2a**) ($x < 1$) and $\{[NP(NHC_6H_4OH)_2]_{x-1}[NPCl(NHC_6H_4OH)]_{2-x}\}_n$ (**2b**) ($x > 1$) that carry terminal OH groups. The reaction of **2a** with NH_2Bu (Bu = *n*-butyl) gave the stable and soluble polymers $\{[NP(NHBu)_2]_{1-x}[NP(NHBu)(NHC_6H_4OH)]_x\}_n$ (**3**). Also, in agreement with the cyclic models, the reaction of *p*-aminophenol with the partially substituted copolymer $\{[NP(O_2C_{12}H_8)]_{0.8}[NPCl_2]_{0.2}\}_n$ occurs only at refluxing temperatures and in the presence of Cs_2CO_3, producing the poly(aryloxyphosphazene) derivative $\{[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_4NH_2)_2]_{0.2}\}_n$ (**4**) possessing terminal NH_2 groups, or, if the chlorine substitution is completed with phenol, the analogous polymer $\{[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_5)(OC_6H_4NH_2)]_{0.2}\}_n$ (**5**).

Introduction

Poly(phosphazene)s,[1] which consist of chains of -N=PX_2- units, are usually prepared by chlorine substitution in the parent poly(dichlorophosphazene) $[NPCl_2]_n$. Many aryloxyphosphazenes of the type $[NP(OC_6H_4R)_2]_n$ can therefore be synthesized by reacting $[NPCl_2]_n$ with phenoxides of the type $NaOC_6H_4R$. However, this method may not be effective in some special cases, for example with bifunctional reagents,[2] or with phenoxides carrying R groups that can also react with the P−Cl bonds, as these reactions could result in crosslinking.[3] The introduction of R groups that could incorporate interesting chemical reactivity to the phosphazenes polymers therefore presents several challenges frequently requiring protection and deprotection synthetic steps.[3]

One of the reactive groups with potential interest is R = NH_2. Although there are reports describing the incorporation of -$OC_6H_4NH_2$ functions to cyclic triphosphazenes directly from $NaOC_6H_4NH_2$,[4] the method most widely used is based on the formation of an -NO_2 derivative, followed by its catalytic reduction to the amine.[3,5−9] Other methods include the hydrolysis of an acetamido precursor.[10]

Previously, we have shown[11] that chlorine substitution reactions in phosphazenes may be carried out using one equivalent of phenol HOC_6H_4R in the presence of M_2CO_3 (M = K or Cs), and that the poly(dichlorophosphazene) $[NPCl_2]_n$ reacts with the bifunctional reagent 2,2′-(HO)C_6H_4-C_6H_4(OH) and K_2CO_3 without crosslinking, affording the phosphazene polymer $[NP(O_2C_{12}H_8)]_n$.[12a] We used the same type of direct reaction with binaphthol and produced the chiral poly(binaphthoxyphosphazene)s.[12b]

The above observations led us to investigate the direct reaction of the bifunctional *p*-aminophenol ($HOC_6H_4NH_2$) with chlorophosphazenes and Cs_2CO_3, and try to activate the OH group selectively with the aim of obtaining uncrosslinked poly(phosphazene)s with terminal -NH_2 groups

[a] Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo
33071 Oviedo, Spain
Fax: (internat.) +34-985/103-446
E-mail: gac@sauron.quimica.uniovi.es

in one step. However, we found that the aminophenol reacts either through the OH or the NH_2 depending on the nature of the chlorophosphazenes and on the reaction conditions.

Results and Discussion

In order to obtain information about the reactivity of *p*-aminophenol ($HOC_6H_4NH_2$) towards chlorophosphazenes under various conditions, we first studied its reactions with two cyclic models: the unsubstituted hexachlorocyclotriphosphazene [$N_3P_3Cl_6$] and the partially substituted spirocyclic derivative bis(2,2′-dioxybiphenyl)dichlorocyclotriphosphazene [$N_3P_3Cl_2(O_2C_{12}H_8)_2$].[12a]

The reaction of $HOC_6H_4NH_2$ (6.1 equiv.) with [$N_3P_3Cl_6$] at room temperature in THF and using K_2CO_3 as a proton abstractor proceeded very slowly and exclusively through the NH_2 group. After 11 days the ^{31}P NMR spectrum of the THF solution showed the presence of two main products (Table 1), which, by comparison with known substituted cyclic aminophosphazenes,[13] could be identified as the geminally tetrasubstituted [$N_3P_3Cl_2(HNC_6H_4OH)_4$] and the hexasubstituted [$N_3P_3(HNC_6H_4OH)_6$] derivatives (for the related species [$N_3P_3(NHC_6H_4OMe)_6$] the value is δ = 6.4). No signals attributable to aryloxyphosphazenes were detected (the well-known [$N_3P_3(OC_6H_4NH_2)_6$] derivative[1d] has a singlet near δ = 11 in THF[5]).

Table 1. ^{31}P NMR spectroscopic data (δ) for the cyclic phosphazenes in THF solution; the data given are the center of the multiplets of the A_2 (pseudo doublet) and M (pseudo triplet) part of the A_2M spin systems, or the singlet of the A_3 spin systems

Derivative	A_2	M	A_3
[$N_3P_3Cl_2(HNC_6H_4OH)_4$]	2.1	23.6	
[$N_3P_3(HNC_6H_4OH)_6$]			5.5
[$N_3P_3Cl_2(O_2C_{12}H_8)_2$]	20.0	28.9	
[$N_3P_3Cl(NHC_6H_4OH)(O_2C_{12}H_8)_2$]	26.5	8.0	
[$N_3P_3(NHC_6H_4OH)_2(O_2C_{12}H_8)_2$]	28.3	2.4	
[$N_3P_3Cl(OC_6H_4NH_2)(O_2C_{12}H_8)_2$]	23.9[a]		
[$N_3P_3(OC_6H_4NH_2)_2(O_2C_{12}H_8)_2$]	26.9	11.8[b]	

[a] This A_2B system shows a complex signal centered at δ = 23.9. In acetone it appears at δ = 24.8. [b] In acetone at δ = 27.5 and 12.6, and in [D_6]DMSO at δ = 26.7 and 12.0.

This conclusion was corroborated by the ^{13}C NMR spectrum (**a** in Figure 1) that showed the presence of free *p*-aminophenol and sharp peaks for the C_6H_4 group at δ = 152.5 (one carbon atom), 133.2 (one carbon atom), 121.1 (two carbon atoms), and 115.0 (two carbon atoms). As will be further discussed below, comparison of these data with those corresponding to various phenols and phosphazene derivatives (Table 2), unambiguously demonstrates that they correspond to aminophosphazenes and not to aryloxyphosphazenes.

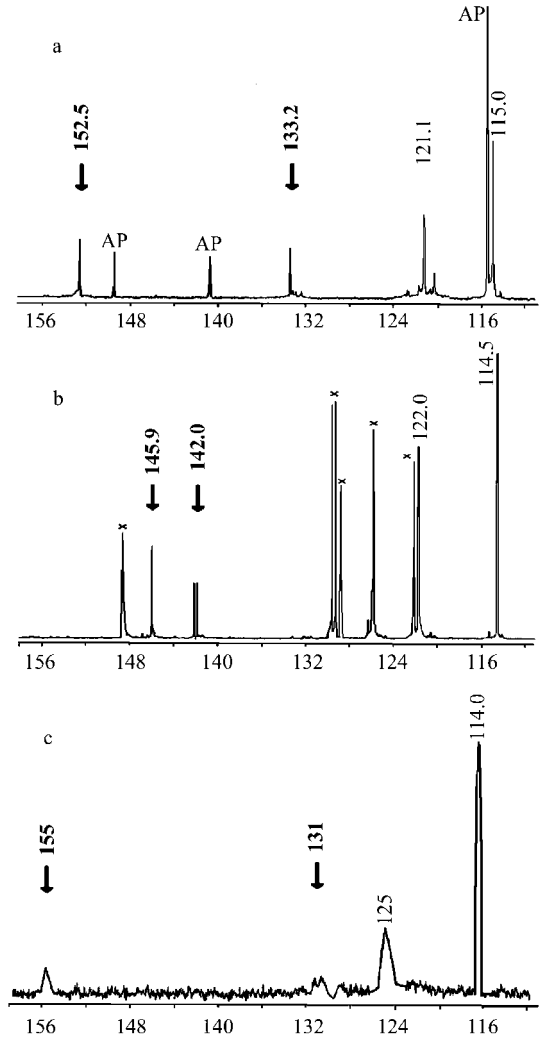
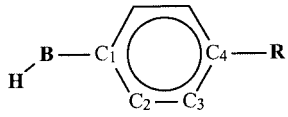
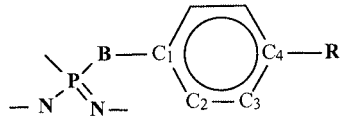


Figure 1. ^{13}C NMR spectra of: 1a) aminophosphazenes formed in the reaction between [$N_3P_3Cl_6$] and *p*-aminophenol in THF at room temperature with K_2CO_3 (AP = signals of the free *p*-aminophenol); 1b) [$NP(OC_6H_4NH_2)_2(O_2C_{12}H_8)_2$] (**1**) in THF (*x* = peaks corresponding to the carbon atoms of the $O_2C_{12}H_8$ group); 1c) THF solution of polymer **2a** (*x* = 0.4)

The data in Table 2 show that when a *para*-disubstituted benzene derivative of the type H-B-C_6H_4-R reacts with a phosphazene P−Cl bond to form -NP-B-C_6H_4-R units, the chemical shift of the carbon bonded to B decreases by ca. 5 ppm, while that of the carbon bonded to R increases by ca. 3 ppm (tendencies consistent with the data for the molecules H-B-C_6H_4-R and those of their E-B-C_6H_4-R derivatives, where E is an electron-withdrawing group[17]). Therefore, starting from *p*-aminophenol $H_2NC_6H_4OH$, for which the weak carbon atom peaks appear (in THF) at δ = 149.2 (C bonded to the OH) and 140.5 (C bonded to the NH_2), the formation of $NP(NHC_6H_4$-OH) units should give two well-separated peaks close to δ = 153 and 135, in complete agreement with the two secondary carbon signals of the products mentioned above, while for the formation of $NP(OC_6H_4$-$NH_2)$ units two very close peaks near δ = 143 would have been expected.

Table 2. ^{13}C NMR chemical shifts of the ring carbon atoms corresponding to the HB-C_6H_4-R molecules and to the A-C_6H_4-B groups bonded to poly(phosphazene); all the spectra were recorded in $CDCl_3$ unless otherwise stated





BH	R	C^1	C^2	C^3	C^4	ref.	C^1	C^2/C^3	C^4	ref.
OH	H	155	115.5	129.8	121.1	23, 24	151.6	121.2/128.8	123.6	25, 26
OH	Me	152.9	115.3	130.2	130.2	23, 24	149.6	121/129.1	132.1	25, 26, 16
OH	OMe	149.7	116.3	115.2	153.5	23, 24	146.1	122.8/114.4	156	27[a]
OH	CN	161.6	116.4	134.2	101.1	23[b]	155	122/134	108	28
OH	F	151.1	116.6	116.3	157.7	24	148	123.1/116.5	160.3[c]	29[a]
OH	Cl	153.8	116.8	129.6	126	23, 24	150.4	122.9/130.2	130.8	29[a]
OH	Br	154.3	117.3	132.6	113.1	23	149.8	122.1/132.2	118	30
OH	I	154.3	117.6	138.2	83.2	this work	150.8	120.2/138.6	89.1	30[d]
OH	C(O)OPr	161.1	115.5	132	122	23	154	120/130.8	126.8	26
OH	PPh_2	157.4	116.4	136.5	128.5	31	152	121.7/ 135.2	134.6 (hidden)	31
SH	Br	132.1	129.9	131.1	119.5	23	128.4	137.3/133	124.4	32
NH_2	H	146.5	115	129.3	118.4	23, 24	141.8	118.6/129.5	121.2	16

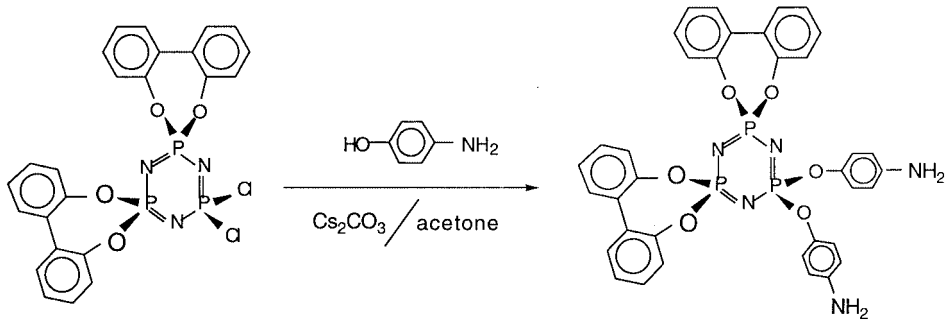
[a] Solvent not available. [b] [D_6]DMSO. as solvent. [c] J_{C-F} = 250 Hz. [d] 1-Methyl-2-pyrrolidinone (NMP) as solvent.

When carried out in refluxing acetone with Cs_2CO_3 as proton abstractor, the reaction of *p*-aminophenol with $[N_3P_3Cl_6]$ was much faster, although in this case both the NH_2 and the OH groups were activated. After one hour the ^{31}P NMR spectrum of the resulting solution showed very broad and complex signals, suggesting polymerized and crosslinked products, among which it was possible to detect some of the sharp peaks corresponding to the aminophosphazenes mentioned above, together with others closer to those expected for aryloxyphosphazenes.

The reaction of *p*-aminophenol (2.1 equivalents) with the dichlorophosphazene cyclic model $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ was also very dependent on the conditions but was much more selective. In THF at room temperature with K_2CO_3, therefore, the process was very slow and occurred selectively, but not exclusively, through the NH_2 group. After 20 days the ^{31}P NMR spectrum showed, in addition to the starting dichlorophosphazene (ca. 14 mol %), the presence of a mixture of $[N_3P_3Cl(NHC_6H_4OH)(O_2C_{12}H_8)_2]$ (65%), $[N_3P_3(NHC_6H_4OH)_2(O_2C_{12}H_8)_2]$ (12%), $[N_3P_3Cl(OC_6H_4NH_2)(O_2C_{12}H_8)_2]$ (5%), and another very weak A_2M spin system with the pseudo-triplet at δ = 13.1 and the pseudo-doublet at δ = 26.4, which could be attributed to the mixed species $[N_3P_3(NHC_6H_4OH)(OC_6H_4NH_2)(O_2C_{12}H_8)_2]$ (1%). The known compound[9] $[N_3P_3(OC_6H_4NH_2)_2(O_2C_{12}H_8)_2]$ (**1**) was not present (see below).

Again, this result was supported by the ^{13}C NMR spectrum of the THF solution, which, in addition to the signals of free aminophenol and those for the $O_2C_{12}H_8$ groups, showed the two expected sharp peaks at δ = 152.4 and 133.3 indicative of the $NP(NHC_6H_4OH)$ units, and two other much weaker signals at δ = 145.5 and 142.3 (doublet) corresponding to the aryloxyphosphazene derivatives.

In contrast, the reaction of *p*-aminophenol with $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ in refluxing acetone and using Cs_2CO_3 as proton abstractor gave first the aryloxyphosphazene intermediate $[N_3P_3Cl(OC_6H_4NH_2)(O_2C_{12}H_8)_2]$ (see Table 1), and finally the known bis(*p*-aminophenoxy)-containing compound $[N_3P_3(OC_6H_4NH_2)_2(O_2C_{12}H_8)_2]$ (**1**) (Scheme 1), which was isolated in good yield. This compound had been obtained previously by hydrogenation of the $-OC_6H_4NO_2$ derivative.[9] No products from the reac-



1

Scheme 1

tion between the P−Cl bonds and the NH_2 groups were observed.

As expected, the ^{13}C NMR spectrum of the *p*-hydroxyaminophosphazene[9](**1**) in THF (see **b** in Figure 1), showed signals for the weak carbon atoms of the C_6H_4 groups at $\delta = 145.9$ and 142.0 (doublet with $J_{P,C} = 7.3$ Hz) (see the Exp. Sect. for NMR spectroscopic data in [D$_6$]DMSO). These data confirmed all the conclusions outlined above and also showed that ^{13}C NMR spectroscopic data are very useful in distinguishing between NP-NHC_6H_4-OH and NP-OC_6H_4-NH_2 units.

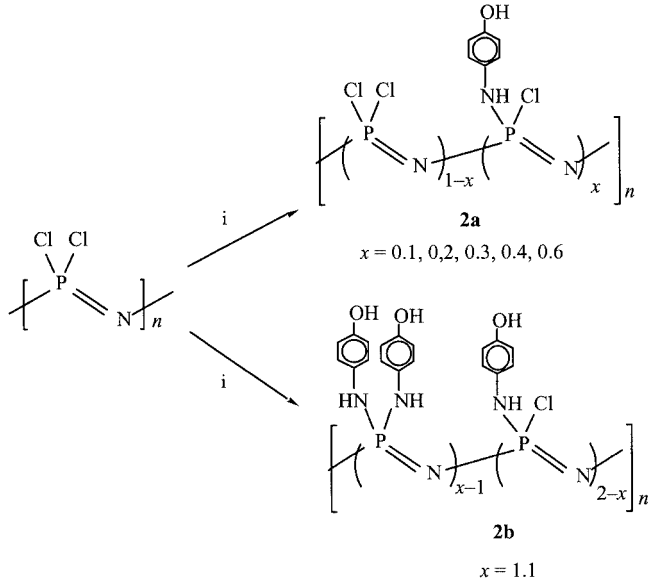
The selectivity of the reactions of *p*-aminophenol with $[N_3P_3Cl_6]$ and $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ under the different conditions used in this work is totally consistent with the experimental knowledge accumulated from the substitution of chlorine atoms in chlorophosphazenes by phenols and amines.

We have established[11] that in refluxing acetone and in the presence of cesium carbonate the reactions of the phenols RC_6H_4OH with chlorocyclophosphazenes are very fast. With K_2CO_3 as proton abstractor they are slower, and in THF as solvent are much slower. Logically, at room temperature they are much slower than at reflux. Also, the phenols where R is an electron-donating group react more slowly. Therefore, in the case of *p*-aminophenol the reactions through the phenolic OH group should be extremely slow in THF at room temperature with K_2CO_3, but much faster in refluxing acetone and with Cs_2CO_3.

The reactions through the NH_2 group are also dependent on the temperature, although they are more affected by steric factors, less sensitive to the solvent and, as expected, they are almost independent of the alkaline carbonate used as proton abstractor. Consistently, the reaction with $[N_3P_3Cl_6]$ in THF at room temperature with K_2CO_3 occurs only through the NH_2 group, i.e., the aminophosphazenes are the expected kinetic products. In refluxing acetone with Cs_2CO_3 the OH becomes sufficiently activated and the *p*-aminophenol reacts through both groups leading to cyclomatrix products. The same effects operate in the case of the $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ derivative, although this compound is less reactive towards substitution than the $[N_3P_3Cl_6]$. Therefore, in THF at room temperature with K_2CO_3 a very slow reaction through the NH_2 group is the main process observed, whereas in refluxing acetone with Cs_2CO_3 the reaction through the OH group becomes sufficiently fast to give the aryloxyphosphazene derivatives exclusively (again under kinetic control).

The overall results from the reactivity of *p*-aminophenol with the cyclic models suggested to us the possibility of synthesizing high molecular weight poly(phosphazene)s with terminal *p*-hydroxyphenylamino or *p*-aminophenoxy groups in one step from *p*-aminophenol and poly(chlorophosphazene)s.

We observed that the reaction of $[NPCl_2]_n$ with x equivalents of $HOC_6H_4NH_2$ per $NPCl_2$ unit ($x < 1$), in THF at room temperature with $1.5x$ equivalents of K_2CO_3 (i in Scheme 2) occurred exclusively through the NH_2 groups, producing solutions of the random copolymers with composition $\{[NPCl_2]_{1-x}[NPCl(NHC_6H_4OH)]_x\}_n$ (**2a**) [$x = 0.1$, 0.2, 0.3, 0.4, 0.6]. Above $x = 1$ the copolymers had the formula $\{[NP(NHC_6H_4OH)_2]_{x-1}[NPCl(NHC_6H_4OH)]_{2-x}\}_n$ (**2b**) ($x > 1$), although, even when using a large excess of the *p*-aminophenol, it was not possible to reach substitution degrees higher than $x = 1.2$, as beyond that point the substitution process became very slow.



Scheme 2. i. nx $HOC_6H_4NH_2$ + K_2CO_3/THF, room temperature

The reaction was faster at reflux, but in this case gave insoluble materials, indicating the activation of the OH groups of the aminophenol and their concomitant crosslinking by reaction with the P−Cl bonds. Consistently, we observed that crosslinking could be favored by working with more concentrated solutions of the reactants, by using a large excess of the alkaline carbonate, or by using Cs_2CO_3 instead (as mentioned previously,[11] this reagent makes the reactions of phenols with chlorophosphazenes much faster). Moreover, solutions of the polymers **2a** are only moderately stable at room temperature, especially in the presence of carbonates, giving rise to gelatinous precipitates on standing for several days. We also checked that on carrying out the reaction in the absence of the K_2CO_3 only half the amount of *p*-aminophenol was incorporated into the polymers **2**, the other half reacting as a proton abstractor to give the ammonium salt.

The ^{31}P NMR spectra of THF solutions of the polymers **2** were consistent with their formulation. Thus, for example, for **2a** ($x = 0.4$) the spectrum (Figure 2) shows three signals: a sharp peak at $\delta = -17.4$, corresponding to the fraction of the $NPCl_2$ groups surrounded by two other $NPCl_2$ units and far from the $NPCl(NHC_6H_4OH)$ units, a very broad signal with a maximum at ca. $\delta = -25$, corresponding to the $NPCl_2$ groups surrounded by two $NPCl(NHC_6H_4OH)$ units; and a broad signal centered at ca. $\delta = -15$, due to the $NPCl(NHC_6H_4OH)$ units. For the other copolymers **2a** the spectra changed depending on the value of x. Thus, the

signal attributable to $NPCl(NHC_6H_4OH)$ varied from $\delta = -15$, when placed between two $NPCl_2$ groups, to $\delta = -7$ for those placed inside two other $[NPCl(NHC_6H_4OH)]$ units. Taking into account that the expected mechanism for the reaction of chlorophosphazenes with aromatic primary amines is non-geminal,[14,15] the fraction of $[NP(NHC_6H_4OH)_2]$ units can be considered negligibly small in **2a**. For **2b** ($x = 1.1$) the corresponding broad signal appeared at $\delta = -13$, in agreement with the reported value for similar bis-aminophosphazenes.[16]

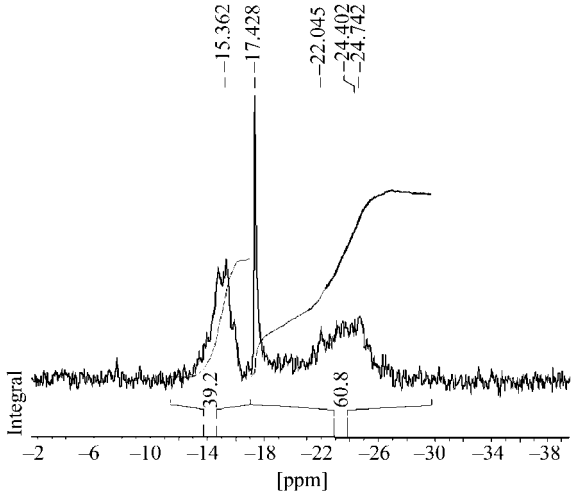


Figure 2. ^{31}P NMR spectrum of **2a** ($x = 0.4$) in THF (see text)

A very valuable proof of the nature of the polymers **2** came from the ^{13}C NMR spectra of the THF solutions (Figure 1c), which showed peaks at $\delta = 155$ (one carbon atom), 131 (one carbon atom), 125 (two carbon atoms) and 116 (two carbon atoms) for the C_6H_4 group, well in agreement with the expected values for NP-NHC_6H_4-OH units and not for NP-OC_6H_4-NH_2 units (see discussion above and Figure 1).

The formation of aminophosphazenes **2** instead of the aryloxyamino derivatives in the reactions of Scheme 2 was also supported by other chemical observations. We found that while the poly(dichlorophosphazene) reacts quickly at room temperature in THF with $NH_2C_6H_4OMe$ and K_2CO_3 to give very similar ^{31}P NMR spectra to those for **2** (the substitution was also incomplete), no reaction occurs with phenol HOC_6H_5 under the same conditions (only in the presence of cesium carbonate and refluxing for 40 hours is the totally substituted polymer obtained[11]). This demonstrates that under the conditions of Scheme 2, the *p*-aminophenol cannot react with $[NPCl_2]_n$ by the OH groups and, therefore, the products observed must be aminophosphazenes.

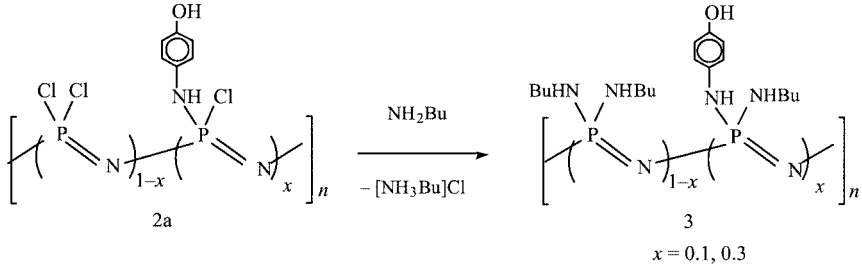
Attempts to use the polymers **2** as precursors for the synthesis of phosphazene copolymers possessing terminal OH groups by reacting them with *p*-substituted phenols (HOC_6H_4R) and cesium carbonate at room temperature were unsuccessful as the replacement of the chlorines by the corresponding phenoxy groups was far too slow to go to completion; heating at reflux led to insoluble products with residual chlorine contents close to 5% by weight.

As described in other cases,[18] however, the polymers **2a** could be stabilized by completing the chlorine substitution with *n*-butylamine (NH_2Bu) (see Scheme 3) to obtain the copolymers $\{[NP(NHBu)_2]_{1-x}[NP(NHBu)(NHC_6H_4OH)]_x\}_n$ (**3**) as stable solids. The chlorine content was very low (0.25%), confirming the complete substitution and ruling out the presence of quaternized ammoniun chlorides. The solubility decreased rapidly as x increased, and therefore polymers with $x > 0.3$ could not be prepared. Moreover, although soluble in THF when freshly prepared, their solubility decreases after some time in the solid state. Occasionally, the solid obtained after the first precipitation step in water (see Exp. Sect.) was sparingly soluble in THF. As the numbers of P−Cl bonds present in the substituted products is negligible, these effects may be attributed to the formation of a three-dimensional net of H-bonding interactions.

All the spectroscopic data for **3a** ($x = 0.3$; see Exp. Sect.) were in agreement with the proposed structure. Thus, the IR spectra showed, together with the expected phosphazene absorptions, a broad intense band centered at 3300 cm^{-1} due to all the -PNHR- units,[13,14,19] and two bands at 1515 and 827 cm^{-1} indicative of the *p*-disubstituted -C_6H_4- group. The latter are less intense in the polymers **3** with $x = 0.1$. The band of the terminal OH group was hidden under the broad absorption of the -PNH- group.

Significantly, as discussed above, the $^{13}CNMR$ spectrum showed, along with the peaks of the NPNHBu group,[18] signals at $\delta = 152.1$ and 136.5 as expected for the groups -$NPNHC_6H_4OH$, the intensity of which increased with x.

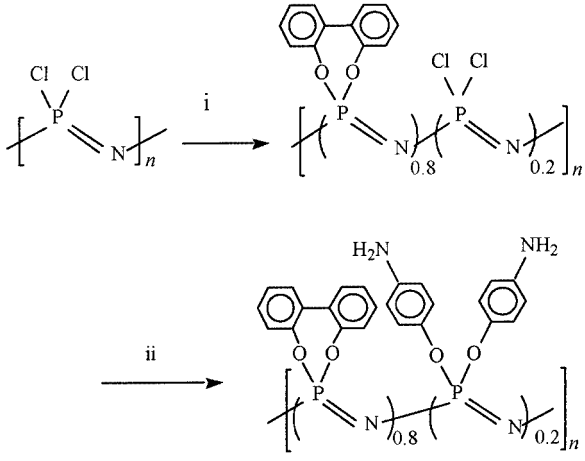
The molecular weight (M_w) of **3a** is of the order of 2×10^5, showing the expected degradation of the chains during reaction with the amine.[18] The thermogravimetric analysis



Scheme 3

(TGA) of **3** showed a decomposition beginning near 70 °C (see Exp. Sect.). This rather low thermal stability may be due, as in the case of other aminophosphazenes,[33] to the elimination of volatile amines. Surprisingly, no well-defined glass transition (T_g) was detected in the differential scanning calorimetry (DSC) curves from −100 °C to 150 °C.

In contrast to the case of $[NPCl_2]_n$, the partially substituted phosphazene copolymer $\{[NP(O_2C_{12}H_8)]_{0.8}[NPCl_2]_{0.2}\}_n$ [12] did not react with *p*-aminophenol at room temperature in the presence of K_2CO_3. Refluxing and the use of Cs_2CO_3 were necessary, although under those conditions, and in agreement with the cyclic models, the reaction occurred exclusively through the OH group to give the aryloxyphosphazene copolymer $\{[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_4NH_2)_2]_{0.2}\}_n$ (**4**) (Scheme 4). Long reflux times and various successive additions of aminophenol were, however, necessary to reach a product with chlorine contents below 0.1%. As a result, the M_w of **4** was only 2.5×10^5, and the yield was low (21%). Moreover, the polymers isolated from different experiments showed that the content of the $NP(OC_6H_4NH_2)_2$ units could be not be perfectly controlled, varying between 0.1 and 0.2, and that on reducing the reaction time with aminophenol the M_w of the products was higher, approaching 8×10^5.



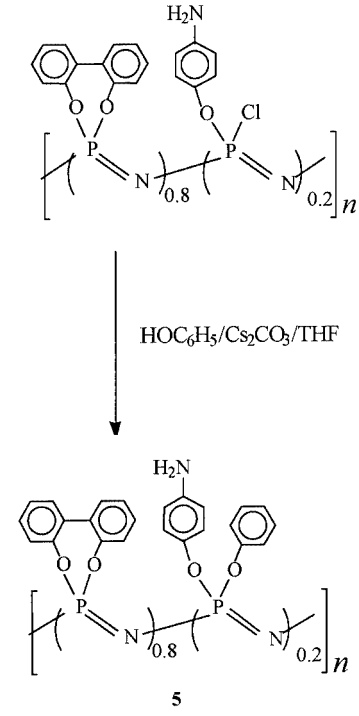
4

Scheme 4. i: HO-C_6H_4-C_6H_4-OH + K_2CO_3 in refluxing THF; ii: HO-C_6H_4-NH_2 + C_2CO_3 in refluxing THF

Clearly, prolonged refluxing in the presence of an excess of aminophenol caused extensive reduction of the chain length, which can be explained by taking into account that the aryloxides may be replaced by anilide ions in phosphazenes,[20] and that the poly(arylaminophosphazene)s are labile to nucleophilic cleavage.[21]

Our attempts to increase the $NP(OC_6H_4NH_2)_2$ units to 40% in the reaction of Scheme 4 resulted in the formation of brown insoluble materials with residual chlorine values of around 0.3% by weight. The known phosphazene polymers $\{[NP(OC_6H_5)_2]_{1-x}[NP(OC_6H_4NH_2)(OC_6H_5)]_x\}_n$ with $x = 0.3$ and 0.7, which have been prepared in high yields by reduction of a *p*-nitrophenoxy precursor,[5,6] are soluble.[5] Therefore, although the presence of the biphenoxy groups may reduce the solubility, it is likely that the insolubility of polymers of type **4** with more than 20% of $NP(OC_6H_4NH_2)_2$ units is due only to crosslinking side reactions during the second step of its synthesis.

These considerations led us to design the synthesis of the polymer $\{[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_5)(OC_6H_4NH_2)]_{0.2}\}_n$ (**5**), shown in Scheme 5, by first forming the intermediate $\{[NP(O_2C_{12}H_8)]_{0.8}[NPCl(OC_6H_4NH_2)]_{0.2}\}_n$ using the precise amount of aminophenol to avoid degradation, and then completing the substitution with HOC_6H_5. The product, isolated in 60% yield, contained only 0.14% residual chlorine and was a stable and soluble white polymer with an M_w of 9×10^5.



5

Scheme 5

All the analytical and spectroscopic properties of the polymers **4** and **5** were consistent with their proposed formulation (see Exp. Sect.). The IR spectra showed the two typical absorptions near 3450 and 3370 cm^{-1} (and another one at 1624 cm^{-1}) characteristic of the terminal NH_2 groups,[9] (also present in the cyclic model **1**) while no absorption for terminal OH was observed.

The ^{31}P NMR spectra showed a broad signal at around $\delta = -6$, characteristic of the skeletal phosphorus atoms of the $[NP(O_2C_{12}H_8)]$ units, which, as discussed elsewhere,[12] shows that the P atoms are part of a seven-membered ring, and a signal near $\delta = -19$ belonging to the $[NP(OC_6H_4NH_2)_2]$ or $[NP(OC_6H_5)(OC_6H_4NH_2)]$ units (for the known polymers $\{[NP(OC_6H_5)_2]_{1-x}[NP(OC_6H_4NH_2)_x]\}_n$, the chemical shift is $\delta = -19$[5,6]). The relative intensities of the two signals agreed well with the averaged formula of the copolymers, and no signals in the region of $\delta = -15$, corresponding to aminophosphazene units $[NP(NHC_6H_4OH)_2]$,[16] were observed.

The ^1H NMR spectra showed a broad signal near δ = 5, also present in the spectrum of **1**, that may be assigned to the NH_2 protons.[9] For the NH protons of the $[NP(NHC_6H_4R)_2]$ units the signal is expected at ca. δ = 3.[19]

The ^{13}C NMR spectrum showed broad peaks at δ = 145 and 142 (in $[D_6]$DMSO), which, as discussed above, correspond to aryloxyphosphazenes with pendant amino groups and not to aminophosphazenes with pendant OH groups. The weak broad signal at δ = 152 unambiguously corresponds to the phenoxy groups, and the intense one at δ = 148 to the abundant biphenoxy groups present in the chains.[12a]

The thermal stability of **4** and **5**, as measured by TGA, is only moderate. Thus, a slow decomposition begins at ca. 100 °C (**4**) or 50 °C (**5**); the residue left at 800 °C was of the order of 50% in both cases (see Exp. Sect.). As in the case of other aryloxyphosphazenes, the thermal decomposition occurs with elimination of volatile cyclic phosphazenes; other organic products also formed.

Because of the presence of dioxybiphenyl phosphazene units and polar NH_2 terminal groups it was expected that the polymers **4** and **5** should have high T_g values. In fact the DSC curves of both polymers showed very well-defined heat capacity steps with T_g = 155 °C for **4** and T_g = 140 °C for **5**.

Conclusion

Polymeric chlorophosphazenes may be selectively reacted in THF with substoichiometric amounts of *p*-aminophenol under kinetic control either at the OH or NH_2 groups, depending on the conditions. The reaction with poly(dichlorophosphazene) at room temperature and with K_2CO_3 occurs exclusively at the NH_2 group producing aminophosphazenes with terminal OH groups. However, if the available P−Cl bonds are not abundant, as is the case with partially substituted aryloxyphosphazene-chlorophosphazene copolymers, the process is very slow at room temperature, and on carrying out the reaction at reflux and in the presence of Cs_2CO_3 it occurs exclusively at the OH of the *p*-aminophenol, producing aryloxyphosphazenes with pendant NH_2 groups. These observations have led to the designed synthesis of phosphazene copolymers containing NHC_6H_4OH or $OC_6H_4NH_2$ groups directly from *p*-aminophenol.

Experimental Section

General Remarks: K_2CO_3 and Cs_2CO_3 were dried at 140 °C prior to use. Acetone was distilled from anhydrous $CaSO_4$. THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with a boiling point in the range 60−65 °C. The diphenol $HOC_6H_4C_6H_4OH$ and *p*-aminophenol $NH_2C_6H_4OH$ were used as purchased (Aldrich). Butylamine was distilled from CaH_2. Hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Fluka) was purified from hot petroleum ether and dried under vacuum. The cyclic phosphazene $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ was prepared as described elsewhere.[12a] The starting polymer $[NPCl_2]_n$ was prepared as described by Magill et al.[22] All the reactions were carried out under dry nitrogen.

The IR spectra were recorded with a Perkin−Elmer Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200 and AC-300 instruments. ^1H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS. $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in Hz. C, H and N analyses were performed with a Perkin−Elmer 240 microanalyzer. Cl analyses were performed by Galbraith laboratories. Unless stated otherwise, the analytical data given for the cyclic phosphazenes correspond to the isolated reaction products without purification. GPC were measured with a Perkin−Elmer apparatus equipped with a model LC 250 pump, a model LC 290 UV, and a model LC 30 refractive index detector. The samples were eluted with a 0.1wt.-% solution of tetra-*n*-butylammonium bromide in THF through Perkin−Elmer PLGel (Guard, 10^5, 10^4 and 10^3 Å) at 30 °C. Approximate molecular weight calibration was obtained using polystyrene standards having narrow molecular weight distributions. T_g values were measured with a Mettler DSC 300 equipped with a TA 1100 computer. TGA were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under a constant flow of nitrogen.

$[N_3P_3(OC_6H_4NH_2)_2(O_2C_{12}H_8)_2]$ (1): $NH_2C_6H_4OH$ (0.33 g, 3.02 mmol) and Cs_2CO_3 (1.59 g, 4.88 mmol) were added to a solution of $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ (0.7 g, 1.22 mmol) in acetone (40 mL) and the mixture was refluxed with stirring for 19 hours to give a brown mixture. The volatile components were evaporated to dryness and the residue was washed successively with 0.5 M aqueous NaOH (3 × 50 mL) and water (2 × 50 mL). The residue was then dissolved in acetone, dried with solid anhydrous Na_2SO_4, filtered, and the solvents evaporated. The pale brown solid was washed with hexane (2 × 40 mL) and dried under vacuum. Yield: 0.78 g (88.9%). $C_{36}H_{28}N_5O_6P_3$ (719.56): calcd. C 60.1, H 3.92, N 9.73; found C 59.4, H 3.95, N 9.15. IR (KBr): $\tilde{\nu}$ = 3437 w, 3341 w (NH_2), 1625 (NH_2), 1230 s, 1173 vs (N=P), 1271 m, 1093 m (POC) cm^{-1}. $^{31}P\{^1H\}$ NMR ($[D_6]$DMSO): δ = 12.02 $[(POC_6H_4NH_2)_2]$, 26.7 [A_2M system, J_{AM} = 90 Hz, $P(O_2C_{12}H_8)$]. ^1H NMR ($[D_6]$DMSO): δ = 7.65 (d, *J* = 7.5, 4 H), 7.51 (dd, *J* = 7.4, 4 H), 7.42 (dd, *J* = 7.5, 4 H), 7.16 (d, *J* = 7.9, 4 H) ($O_2C_{12}H_8$), 6.96 (d, 4 H), 6.63 (d, *J* = 8, 4 H, OC_6H_4-N), 5.10 (br. s, NH_2). $^{13}C\{^1H\}$ NMR ($[D_6]$DMSO): δ = 147.2 (t), 130.1, 129.7, 127.9, 126.4, 121.6 ($O_2C_{12}H_8$), 146.4, 140.1 (d, $J_{P,C}$ = 7.3), 121.1 (d, $J_{P,C}$ = 4.1), 114.2 ($OC_6H_4NH_2$).

THF Solutions of $\{[NPCl_2]_{1-x}[NPCl(NHC_6H_4OH)]_x\}_n$ (2a) ($x < 1$), $\{[NP(NHC_6H_4OH)_2]_{x-1}[NPCl(NHC_6H_4OH)]_{2-x}\}_n$ (2b) ($x > 1$): $NH_2C_6H_4OH$ (0.94*x* g, 8.6*x* mmol) and K_2CO_3 (1.78*x* g, 12.9*x* mmol) were added to a solution of $[NPCl_2]_n$ (1 g, 8.6 mmol) in THF (200 mL) and the mixture was mechanically stirred for 10 hours ($x < 1$) or 40 hours ($x > 1$) at room temperature.

The ^{31}P NMR spectrum of the solutions of **2a** showed two groups of signals having maxima that depended on *x*, one in the region of δ = −25 to −17 ($NPCl_2$) and the other in the range δ = −15 to −7 [$NPCl(NHC_6H_4OH)$] with relative intensities (1 − *x*):*x*. For **2b** (x = 1.1) the ^{31}P NMR spectra showed a broad signal at δ = −13 attributable to $[NP(NHC_6H_4OH)_2]$ besides the [$NPCl(NHC_6H_4OH)$] signal at δ = −7.

The ^{13}C NMR of the solutions showed peaks at δ = 155, 131, 125 and 116.

The solutions were unstable on standing for several days, especially if heated, giving rise to a gelatinous precipitate.

$\{[NP(NHBu)_2]_{0.7}[NP(NHBu)(NHC_6H_4OH)]_{0.3}\}_n$ (3a): $NH_2C_6H_4OH$ (0.40 g, 3.66 mmol) and K_2CO_3 (0.60 g, 4.34 mmol) were added to a solution of $[NPCl_2]_n$ (1.40 g, 12.1 mmol) in THF (150 mL), and the mixture was stirred mechanically for 18 hours at room temperature. NH_2Bu (24.4 mL, 18.06 g, 246.9 mmol) was then added at 0 °C, the mixture stirred at this temperature for 30 minutes, and then for another 125 hours at room temperature. After adding 150 mL of THF, the mixture was filtered through celite, concentrated, and added to 1.5 L of water. The resulting fibrous, pink precipitate was washed with water (2 × 1.5 L) and the solid was dried overnight in a desiccator containing P_2O_5 at reduced pressure. The product was dissolved in THF (400 mL) and filtered through activated carbon to eliminate the pink color. The resulting solution was concentrated and added to hexane (1.5 L). The final solid was filtered and dried under vacuum at room temperature for two days. Yield: 1.42 g (59%). $C_{8.6}H_{18.8}N_3O_{0.3}P$ (200.03): calcd. C 51.6, H 9.47, N 21.0; found C 49.7, H 8.82, N 20.3. Chlorine content 0.25%. IR (KBr): $\tilde{\nu}$ = 3334 s, br., (NH), 1515 s, 827 s, (*p*-C6H4-), 1256 s, 1209 vs (N=P), 1118, 1093 m (PNC) cm^{-1}. $^{31}P\{^1H\}$ NMR ([D$_8$]THF): δ = 4.5 [NP(NHBu)$_2$], −3.7 [br. m, NP(NHC$_6$H$_4$OH)(NHBu)]. ^1H NMR ([D$_8$]THF): δ = 7.5 (OH), 7.16, 6.65 (br. m, C$_6$H$_4$), 3.01 (CH$_2$-NH), 2.67 (NH), 1.5 (br. m, -CH$_2$CH$_2$-), 1.05 (br. m, CH$_3$-). $^{13}C\{^1H\}$ NMR ([D$_8$]THF): δ = 152.1, 136.5, 120.0 (2 C), 116.1 (2 C), (C$_6$H$_4$), 41.5, 34.6, 20.8, 14.4 (NHBu). M_w (GPC): 230 000, M_w/M_n = 3.7. TGA: Continuous weight loss from 70 °C, with two fast stages at 220 °C (−32%) and 640 °C (−58%). Final residue at 800 °C: 2.2%.

Other polymers $\{[NP(NHBu)_2]_{1-x}[NP(NHBu)(NHC_6H_4OH)]_x\}_n$ with x between 0.1 and 0.3 were prepared similarly using $NH_2C_6H_4OH$ (1.32x g, 12.1x mmol), K_2CO_3 (2.0x g, 14.5x mmol) and NH_2Bu (273x mL, 202x g., x mmol). The yield was of the order of 50%. The compounds were sometimes slightly pink and lost their solubility on standing. On occasions the solid obtained from the first precipitation in water was only sparingly soluble. In all cases, the chlorine contents were of the order of 0.26% and the M_w (GPC) of ca. 500 000.

$[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_4NH_2)_2]_{0.2}\}_n$ (4): 2,2′-Biphenol (2.39 g, 12.84 mmol) and K_2CO_3 (7.1 g, 51.37 mmol) were added to a solution of $[NPCl_2]_n$ (1.86 g, 16.05 mmol) in THF (200 mL), and the mixture was refluxed with mechanical stirring for 24 hours. $NH_2C_6H_4OH$ (1.4 g, 12.83 mmol) and Cs_2CO_3 (4.18 g, 12.83 mmol) were then added and the refluxing was continued for 24 hours (t_1). More *p*-aminophenol (1.4 g, 12.83 mmol) was added to the resulting mixture and refluxing was further continued for 24 hours (t_2). Following the same procedure as above, the polymer **4** was isolated as a pale brown solid that was dried for three days under vacuum at 20 °C. Yield: 0.8 g (21%). $C_{12}H_{8.8}N_{1.4}O_2P$ (235.58): calcd. C 61.2, H 3.76, N 8.32; found C 61.1, H 3.45, N 7.71. Chlorine content 0.08%. IR (KBr): $\tilde{\nu}$ = 3440 w, 3372 w (NH_2), 1624 w (NH_2), 1247 s, 1194 vs (N=P), 1272 m, 1096 m (POC) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −5.9 [br. m, P(O$_2$C$_{12}$H$_8$)], −19.4 (br. m, P-OC$_6$H$_4$-). ^1H NMR ($CDCl_3$): δ = 7.4−6.6 (br. m, aromatic rings), 6.2 (NH_2). $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 148, 129, 128, 125, 122 (O$_2$C$_{12}$H$_8$), 145, 142, 121, 114 (OC$_6$H$_4$NH$_2$) (all broad). M_w (GPC): 250 000, M_w/M_n = 3.2. T_g (DSC) = 155 °C. ΔC_p = 0.30 J[gK]$^{-1}$. TGA: Decomposition begins at 100 °C (−3.5%). It is fast at 300 °C (−14%) and very fast at 400 °C. Final residue at 800 °C: 53%.

The same experimental procedure, but with t_1 = 48 h and t_2 = 30 h, gave a more soluble polymer in 43% yield as a pale brown solid having the formula $[NP(O_2C_{12}H_8)]_{0.9}[NP(OC_6H_4NH_2)_2]_{0.1}\}_n$. $C_{12}H_{8.4}N_{1.2}O_2P$ (232.37): calcd. C 62.0, H 3.64, N 7.2; found C 62.5, H 3.59, N 6.91. Chlorine content 0.05%. M_w (GPC): 800.000, M_w/M_n = 4.2. T_g (DSC) = 155 °C, ΔC_p = 0.26 J[gK]$^{-1}$.

$[NP(O_2C_{12}H_8)]_{0.8}[NP(OC_6H_5)(OC_6H_4NH_2)]_{0.2}\}_n$ (5): 2,2′-biphenol (1.95 g, 10.47 mmol) and K_2CO_3 (5.8 g, 42.0 mmol) were added to a solution of $[NPCl_2]_n$ (1.52 g, 13.1 mmol) in THF (200 mL), and the mixture was refluxed with mechanical stirring for 25 hours. $NH_2C_6H_4OH$ (0.81 g, 7.46 mmol) and Cs_2CO_3 (2.43 g, 7.46 mmol) were then added and the refluxing was continued for another 40 hours. HOC_6H_5 (0.5 g, 5.31 mmol) and more Cs_2CO_3 (1.73 g, 5.31 mmol) were added to the mixture, and refluxing was continued for a further 23 h. Following the same procedure as above, the polymer **5** was isolated as a white solid that was dried for three days under vacuum at 20 °C. Yield: 1.9 g (62%). $C_{12}H_{8.6}N_{1.2}O_2P$ (232.57): calcd. C 62.0, H 3.73, N 7.23; found C 61.8, H 3.92, N 7.43. Chlorine content 0.14%. IR (KBr): $\tilde{\nu}$ = 3451 w, 3374 w (NH_2), 1624 (NH_2), 1247 s, 1193 vs (N=P), 1272 m, 1096 m (POC) cm^{-1}. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ = −5.9 [br. m, P(O$_2$C$_{12}$H$_8$)], −20.0 (br. m, P-OC$_6$H$_4$-). ^1H NMR ($CDCl_3$): δ = 7.4−6.6 (br. m, aromatic rings), 6.2 (NH_2). $^{13}C\{^1H\}$ NMR ([D$_6$]DMSO): δ = 148, 129, 128, 125, 122 (O$_2$C$_{12}$H$_8$), 152, 120 (OC$_6$H$_5$), 145, 142, 121, 114 (OC$_6$H$_4$NH$_2$) (all broad). M_w (GPC): 900 000. M_w/M_n = 4.3. T_g (DSC) = 140 °C. ΔC_p = 0.28 J[gK]$^{-1}$. TGA: Decomposition begins at 40 °C and is continuous, gets faster at 125 °C and at 350 °C is very fast. Residue at 800 °C: 49%.

Acknowledgments

We are grateful to the Spanish FYCIT (Project PBMAT-98) and DGITYT (Project PB98) for financial support.

[1] [1a] J. E. Mark, H. R. Allcock, R. West, *Inorganic Polymers*, Prentice Hall, Engelwood Cliffs, N.J., USA, **1992**. [1b] I. Manners, *Angew. Chem. Int. Ed. Engl.* , **1996**, *35*, 1602−1621. [1c] C. W. Allen, *Coord. Chem. Rev.* **1994**, *130*, 137−173. [1d] R. de Jaeger, M. Gleria, *Prog. Polym. Sci.* **1998**, *23*, 179−276.
[2] H. R. Allcock, *Chem. Mater.* **1994**, *6*, 1476−1491.
[3] H. R. Allcock, *Appl. Organomet. Chem.* **1998**, *12*, 659−666.
[4] M. D. Bezoari. US Patent 4,864,047, 05 Sept. **1989**; **1990**, *113*, 24242h.
[5] H. R. Allcock, P. E. Austin, T. F. Rakowsky, *Macromolecules* **1981**, *14*, 1622−1625.
[6] H. R. Allcock, W. C. Hymer, P. E. Austin, *Macromolecules* **1983**, *16*, 1401−1406..
[7] R. Bertani, G. Facchin, M. Gleria, *Inorg. Chim. Acta* **1989**, *165*, 73−82.
[8] D. Kumar, T. L. ST Clair, *Polyhedron* **1992**, *11*, 1671−1678.
[9] D. Kumar, A. D. Gupta, *Macromolecules* **1995**, *28*, 6323−6329.
[10] S-K. Kwon, *Bull. Korean Chem. Soc.* **2000**, *21*, 969−972.
[11] G. A. Carriedo, F. J. García Alonso, P. A. González, *Macromol. Rapid Commun.* **1997**, *18*, 371−377.
[12] [12a] G. A. Carriedo, L. Fernández-Catuxo, F. J. García Alonso, P. Gómez Elipe, P. A. González, *Macromolecules* **1996**, *29*, 5320−5325. [12b] G. A. Carriedo, F. J. García Alonso, P. A. González, J. L. García Alvarez, *Macromolecules* **1998**, *31*, 3189−3196..
[13] S. Ganapathiappan, S. S. Krishnamurthy, *J. Chem. Soc., Dalton Trans.* **1987**, 579−584.
[14] S. Ganapathiappan, S. S. Krishnamurthy, *J. Chem. Soc., Dalton Trans.* **1987**, 585−590.
[15] C. W. Allen, *Chem. Rev.* **1991**, *91*, 119−135.
[16] H. R. Allcock, R. J. Fitzpatrick, L. Salvati, *Chem. Mater.* **1991**, *3*, 1120−1132.

[17] H.-O. Kalinowski, S. Berger, S. Braun, *Carbon-13 NMR Spectroscopy*, J. Wiley & Sons, New York, **1988**, p. 313 ff.
[18] M. N. Nobis, A. R. McWilliams, O. Nuyken, I. Manners, *Macromolecules* **2000**, *33*, 7707−7712.
[19] J. Y. Chang, S. B. Rhee, S. Cheong, M. Yoon, *Macromolecules* **1992**, *25*, 2666−2670.
[20] H. R. Allcock, L. A. Smeltz, *J. Am. Chem. Soc.* **1976**, *98*, 4143−4149.
[21] J. E. White, R. E. Singler, S. A. Leone, *J. Polym. Sci. Polym. Chem. Ed.* **1975**, *13*, 2531−2543.
[22] A. N. Mujumdar, S. G. Young, R. L. Merker, J. H. Magill, *Macromolecules* **1990**, *23*, 14−21.
[23] *Integrated Spectroscopic data Base System for Organic Compounds*, National Institute of Materials and Chemical Research, Tsukuba, Ibaraki 305−8565, Japan. (http://www.aist.go.jp/RIODB/SDBS/sdbs/owa/sdbs_sea.cre_frame_sea).
[24] W. Bremser, L. Ernst, B. Franke, R. Gerhards, A. Hardt, *Carbon-13 NMR Spectral data in Machine Readable Form*, Verlag Chemie, Weinheim, **1981**.
[25] H. R. Allcock, C. J. Nelson, W. D. Coggio, *Chem. Mater.* **1994**, *6*, 516−524.
[26] H. R. Allcock, C. T. Morrissey, W. K. Way, N. Winograd, *Chem. Mater.* **1996**, *8*, 2730−2738.
[27] A. Medici, G. Fantin, P. Pedrini, M. Gleria, F. Minto, *Macromolecules* **1992**, *25*, 2569−2574.
[28] M. A. Gómez, C. Marco, J. M. Gómez Fatou, G. A. Carriedo, F. J. García Alonso, P. Gómez Elipe, *Eur. Polym. J.* **1996**, *32*, 717−723.
[29] S. G. Young, M. Kojima, J. H. Magill, F. T. Lin, *Polymer* **1992**, *33*, 3215−3225.
[30] M. A. Olshavsky, H. R. Allcock, *Macromolecules* **1995**, *28*, 6188−6197.
[31] G. A. Carriedo, F. J. García Alonso, P. A. González, P. Gómez-Elipe, *Polyhedron* **1999**, *18*, 2853−2859.
[32] G. A. Carriedo, J. Jiménez, P. Gómez Elipe, F. J. García Alonso, *Macromol. Rapid. Commun.* **2001**, *22*, 444−447.
[33] H. R. Allcock, G. S. McDonnell, G. H. Riding, I. Manners, *Chem. Mater.* **1990**, *2*, 425−432.

Received August 10, 2001
[I01308]