The Controlled and Regioselective Macromolecular Nitration of Poly(2,2′-dioxy-1,1′-biphenylphosphazene) in Concentrated Sulfuric Acid

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ABSTRACT: The polyphosphazene $[NP(O_2C_{12}H_8)]_n$ (**1**) $[(O_2C_{12}H_8) = $ 2,2′-dioxy-1,1′-biphenyl] was reacted with different molar ratios of 65% aqueous HNO_3 (or with $LiNO_3$) in concentrated (98%) sulfuric acid under different experimental conditions to give the nitrated polymers 5,5′-3,3′-$\{NP[O_2C_{12}H_{8-x}(NO_2)_x]\}_n$ (**2**) ($x = 0.2$ to 2) opening the route to further functionalization of (**1**) directly in the dioxy-biphenyl-phosphorus cyclic units. The reaction was not perfectly randomized and was not regiospecific but showed high regioselectivity in favor of the 5,5′ positions. The glass transitions of the products (in the range 161−238 °C) showed a linear dependence with the NO_2 contents evidencing the lack of chemical regularity along the chains. The TGA thermograms of the nitrated polymers showed that the decompositions were faster the higher the NO_2 contents leaving less final residue at 800 °C, demonstrating the destabilizing effects of the NO_2 on the polyphosphazene. Various attempts to reduce the NO_2 groups to NH_2 are also described.

Introduction

The incorporation of useful chemical functions to linear polyphosphazenes or their surfaces is a subject of increasing interest and very relevant to the design of materials with predetermined properties including the inmobilization of enzimes.[1] The chemical derivatization of polyphosphazenes by secondary reactions on side groups[1−7] is an important alternative to the classical macromolecular substitution for the introduction of functionalized groups on the polymeric chains. In some cases, however, the chemical derivatization may lead to polymers with irregular structures or even to heterogeneous mixtures and therefore, under favorable conditions, the macromolecular substitution may be advantageous.[8] Examples are the sulfonation of aryloxyphosphazenes[8] and the introduction of pendant PPh_2 ligands.[9] In fact, the nature of the final products of the macromolecular chemical derivatization is highly sensitive to both the electronic and steric effects that govern the regio- and stereochemistry of the reactions involved, and those effects depend critically on the structure and bonding of the starting polymers.

In earlier works we described the synthesis of phosphazene random copolymers of formulas $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(OR)_2]_x\}_n$ (**1b**), $\{[NP(O_2C_{20}H_{12})]_{1-x}[NP(OR)_2]_x\}_n$ (**1c**) (Chart 1) and other derivatives having phosphorus-dioxy-biphenyl or chiral binaphthyl cycles combined biaryloxy or amino phosphazene units carrying a variety of chemical functions R including amines, esters, carboxylic acids, polyamide chains, and also ligands and their transition metal complexes.[10] Those polymers are readily obtained by macromolecular substitution from the corresponding chlorine containing phosphazene precursors such as $\{[NP(O_2C_{12}H_8)]_{1-x}[NPCl_2]_x\}_n$, that for $x < 0.5$ are sufficiently resistant to hydrolysis to be isolated as useful starting materials.[11] However, the attachment of chemical functions directly to the cyclic dioxy-biphenyl-phosphorus by the chemical derivatization of the parent polymer $[NP(O_2C_{12}H_8)]_n$ (**1**) (Chart 1) remains unexplored. Therefore, we have initiated the study of the chemical reactivity of (**1**), a polymer that can be easily prepared[12] even in large quantities,[12d] with averaged M_w that could be adjusted thermally[13] or by acidic degradation[14] within the wide interval 10^6−10^4 (Chart 1). Polymer (**1**) exhibits an unusually large T_g (161 °C) and behaves as a random coil in solution.[15] Herein we wish to report on the regiochemistry of the controlled macromolecular nitration of the $NP(O_2C_{12}H_8)$ units following a method that was successfully used to nitrate low M_w phenyl phosphazenes,[16] or the surface of diphenoxy phosphazenes[17] but taking advantage of the unusual and high solubility of (**1**) in concentrated sulfuric acid where it is perfectly stable. The introduction of NO_2 groups is also interesting because it opens a facile route to further functionalization.

Experimental Section

The HNO_3 (65%) and H_2SO_4 (98%) acids were from Merck. The samples of the polymer $[NP(O_2C_{12}H_8)]_n$ (**1**) used in this study were prepared from $[NPCl_2]_n$ following the method described in ref 12c. The molecular weight distributions (GPC) were similar, having average M_w in the range $0.2-0.8 \times 10^6$ and polydispersity indexes around 3.0. Their purity was checked by C, H, N analysis and ^{31}P, ^1H NMR and IR spectroscopies. The T_g values were all 161 °C.

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded at room temperature on Bruker NAV-400, DPX-300, AV-400 and AV-600 instruments. The ^1H and $^{13}C\{^1H\}$ NMR spectra in d_6-DMSO are given in δ relative to TMS (DMSO at 2.51 ppm and 40.2 ppm respectively). $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. The C, H, N, analyses were performed with an Elementar Vario Macro. GPC were measured with Perkin-Elmer equipment 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 0.1% by weight 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 were obtained using narrow molecular weight distribution polystyrene standards. T_g values were measured with a Mettler DSC Toledo 822 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analyses were performed on a Mettler Toledo TG 50 TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under constant flow of nitrogen. X-ray diffractograms were measured with PANa-

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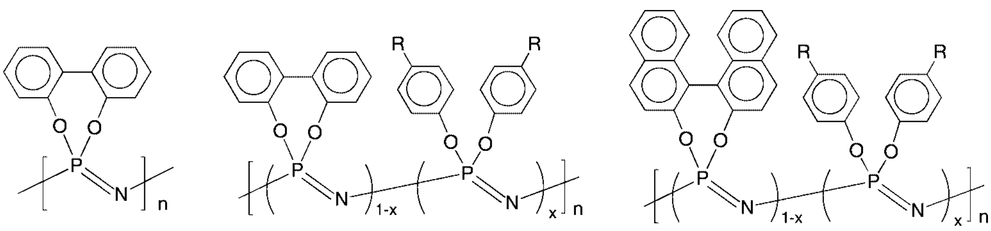
Chart 1. Functionalized Phosphazene Random Copolymers Obtained by Macromolecular Substitution



1 **1b** **1c**

lytical X'Pert Pro, using Kα_1 Cu radiation (1.5406 Å) at 45 kV−40 mA, with an X'Celerator detector with 2.122°. The scans were $\theta/2\theta$ from 2 to 560° 2θ at 0.033° intervals at 300 s per interval.

Preparation of $\{NP[O_2C_{12}H_{8-x}(NO_2)_x]\}_n$ (2) by Nitration of 1. The following preparation for **2**, $x = 0.2$, is representative of the other derivatives but using $0.3x$ mL of the 95% HNO_3 acid per gram of **1**.

To a solution of $[NP(O_2C_{12}H_8)]_n$ (**1**) (2 g, 8.72 mmol) in 98% H_2SO_4 (30 mL) was added 65% (14.5 M) HNO_3 (0.12 mL, 1.74 mmol), and the mixture was stirred for 1.5 h at room temperature. Then it was poured dropwise into water (1 L) with stirring to give a yellow precipitate, which was washed with water until pH = 7. Then product was washed with isopropyl alcohol (300 mL) and diethyl ether (200 mL) and dried in vacuum for one night to give $\{NP[O_2C_{12}H_{7.8}(NO_2)_{0.2}]\}_n$ (**2**, $x = 0.2$) (1.96 g, 93%).

Anal. Calcd for $C_{12}H_{7.8}O_{2.4}N_{1.2}P$ ($M = 238$): C 60.5, H 3.27, N 7.1. Found: C 60.0 H 3.10, N 7.10.

IR (KBr) cm^{-1}: 3066, 3030 vw (ν_{CH} arom), 1606 w, 1584 vw (ν_{CC} arom), 1527 m (NO_2), 1501 m, 1478 s (ν_{CC} arom), 1377 sh m (not assigned), 1348 s (NO_2), 1270 vs, 1246 vs, 1193 vs (ν_{NP}), 1184 w, 1096 s (ν_{P-OC}), 1039 w, 1013 w (not assigned), 953 s br, 917 s (δ_{POC}), 870 w, 808 vw (not assigned), 786 s, 751 s (CH arom), 716 m, 609 m, 590 w, 536 m br (other). Intensity factor I_{1527}/I_{1478} = 0.78.

M_w (GPC): 140,000 (IPD = 4.0).

^{31}P NMR (ppm, DMSO): −5.5 br.

^1H NMR (ppm, DMSO): 7.4 vbr, 7.1 br, 6.7 vbr.

^{13}C NMR (ppm, DMSO): 151, 148.5, 144.7, 135.8, 130.1, 129.1, 126, 122.6.

TGA: −2% (20−300 °C); −40% (300−600 °C, centered at 450 °C); −5% (600−800 °C). Further loss of 5% after 1/2 h at 800 °C. Final stabilized residue at 800 °C: 48%.

T_g = 169 °C, ΔC_p = 0.13 J/g K.

Data for the Other $\{NP[O_2C_{12}H_{8-x}(NO_2)_x]\}_n$. The x values given are those more consistent with the CNH analytical data.

$x = 0.24$. IR(I_{1527}/I_{1478}) = 0.8. T_g = 171 °C

$x = 0.54$. IR(I_{1527}/I_{1478}) = 1.1. T_g = 176 °C.

$x = 0.75$. IR(I_{1527}/I_{1478}) = 1.2. T_g = 186 °C

$x = 0.91$. IR(I_{1527}/I_{1478}) = 1.4. T_g = 189 °C

$x = 0.96$. IR(I_{1527}/I_{1478}) = 1.4. T_g = 186 °C

$x = 0.98$, Obtained in Saturated Solution. IR(I_{1527}/I_{1478}) = 1.4. T_g = 171 °C

$x = 1.40$. IR(I_{1527}/I_{1478}) = 1.5. T_g = 215 °C

$x = 1.65$. IR(I_{1527}/I_{1478}) = 1.6. T_g = 228 °C

$x = 1.80$. IR(I_{1527}/I_{1478}) = 1.8. T_g = 232 °C

$x = 1.92$. IR(I_{1527}/I_{1478}) = 1.9. T_g = 234 °C

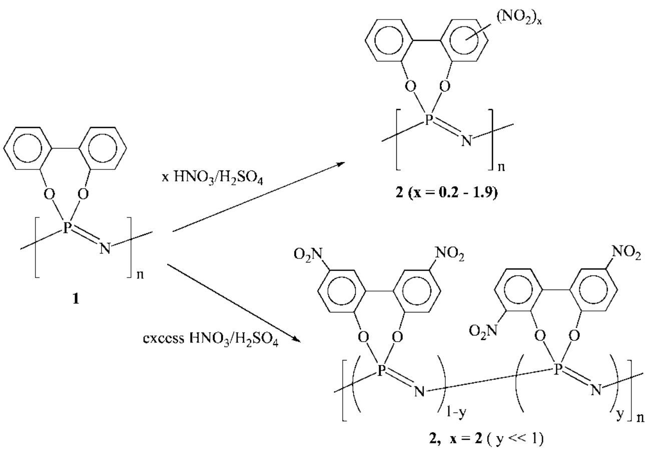
($x = 1.94$. IR(I_{1527}/I_{1478}) = 1.9. T_g = 236 °C

$x = 1.96$. IR(I_{1527}/I_{1478}) = 2.0. T_g = 231 °C

$x = 2.0$. IR(I_{1527}/I_{1478}) = 1.9. T_g = 234 °C

Preparation of $\{NP[O_2C_{12}H_6(NO_2)_2]\}_n$ (2, $x = 2$). Polymer (**1**) (1 g, 4.36 mmol) in 98% H_2SO_4 (25 mL) that was cooled to 0 °C and 65% HNO_3 (1.5 mL, 21.8 mmol) were added, and the mixture was stirred at room temperature for 1.5 h. Then it was poured dropwise into water (1.5 L) with stirring to give a yellow precipitate, which was washed with water until pH = 7. Then product was washed with isopropyl alcohol (300 mL) and diethyl ether (200 mL) and dried in vacuum for one night. Yield 1.32 g, 95%.

Scheme 1



Similar results were obtained increasing the ratio of HNO_3 to 7:1, or at 0 °C overnight. The drying can also be made in vacuum at 50−70 °C overnight.

Anal. Calcd for $C_{12}H_6O_6N_3P$ ($M = 319$): C 45.1, H 1.88, N 13.2. Found: C 43.3, H 1.90, N 13.1.

IR: IR (KBr) cm^{-1}: 3085 w (ν_{CH} arom), 1622 w, 1576 w (ν_{CC} arom), 1528 s (NO_2), 1494 m, 1475 m (ν_{CC} arom), 1377 sh m (not assigned), 1350 vs (NO_2), 1309 m, 1241 vs, 1195 vs (ν_{NP}), 1120 w, 1090 m (ν_{P-OC}), 1040 vw (not assigned), 949 m vbr, (δ_{POC}), 862 m, 841 m, 803 w (not assigned), 786 m, 739 m (CH arom), 716 vw, 665 w, 636 m, 568 m (other). Intensity factor I_{1528}/I_{1475} = 1.9.

^{31}P NMR (ppm, DMSO): −4.5 br.

^1H NMR (ppm, DMSO): 7.9 vbr, 7.6 sh, br, 7.4 br, 6.9 vbr.

^{13}C NMR (ppm, DMSO): 151, 148, 146.8, 145.1, 133.3, 132 (sh), 127, 126 vbr, 123.3 br, 121, 116.8 br.

TGA: −3% (20−300 °C); −26% (300−450 °C, centered at 380 °C); −25% (continuous loss 450−800 °C). Further loss of 13% after 1/2 h at 800 °C. Final stabilized residue at 800 °C: 33%.

T_g = 238 °C, ΔC_p = 0.23 J/g K.

Results and Discussion

The addition of different amounts of concentrated nitric acid (65%) to polymer (**1**) [x mmol of HNO_3 per repeating unit $NP(O_2C_{12}H_8)$ dissolved in concentrated sulfuric acid (98%) at room temperature gave, in 1.5 h, the nitrated copolymers $\{NP[O_2C_{12}H_{8-x}(NO_2)_x]\}_n$ (**2**) (x = 0.2 to 1.9) in more than 90% yield (Scheme 1). Using an excess of HNO_3 (5:1 in mol) afforded the dinitrated polymer $\{NP[O_2C_{12}H_6(NO_2)_2]\}_n$ (**2**, x = 2). Similar results were obtained at 0 °C giving **2**, x = 2, overnight (in 1.5 h at 0 °C the nitration reached x = 1.8). No further nitration was observed increasing the HNO_3 molar ratio to 7:1 or the reaction time to 15 h at room temperature. It is important to notice that no signs of chemical changes were found (by CHN analysis, IR, ^1H, ^{31}P and ^{13}C NMR) after maintaining **1** in H_2SO_4 solution for 3 months at room temperature. Only the expected[14] decrease in the average M_w was confirmed. It was also checked that stirring a suspension of (**1**) in concentrated aqueous HNO_3 at room temperature for 1 to 24 h led only to a similar decrease in the average M_w to 60,000−34,000, without any changes in the analytical and spectroscopic data. Total decomposition with evolution of NO and NO_2 took place, however, when the suspension of **1** in the aqueous HNO_3 was heated at the refluxing temperature for 2 h.

The polymers **2** were isolated as yellow solids mainly amorphous, as shown by a wide halo centered at 21.4° in the X-ray diffraction spectra measured at room temperature, but having a small fraction of a mesophase as evidenced by a weak broad signal at $7 \pm 0.5°$, corresponding to an interplanar spacing of *ca.* 12.5 Å, that was almost independent of *x* [for polymer **1** the spacing is 2.1 Å].[12b]

The limited solubility in THF of the nitrated polymers **2** for $x > 0.2$ prevented an accurate measurement of their M_w by GPC. The values obtained varied from 150,000 to 300,000, well above the expected ones (*ca.* 50,000) originated by the action of the H_2SO_4 acid (see above). However, it is well established that comparison of GPC-M_w of polyphosphazenes of different compositions is not always significant, because of the different tendencies to adopt nonextended conformations or even to form aggregates in solution,[18] and the latter effect is highly probable in the case of **2**. In fact, it has been pointed out that strong intermolecular $\pi-\pi$ stacking interaction are to be expected in both **1** and their derivatives.[19]

The extent of the nitration of the polymers **2** could be accurately determined by CHN analysis, specially the % N contents, and also spectroscopically (see Experimental Section), to confirm that the actual *x* values found were very close to the expected from the ratio of the reactants.

The IR spectra exhibited, together with all the bands required for polyphosphazene polymers with dioxybiphenyl rings, the two strong ν-NO_2 absorptions[20] at 1527 and 1348 cm^{-1}, the intensity of which increased with the degree of nitration. Furthermore, the ratio of the intensities of the bands at 1527 and 1478 cm^{-1} correlated linearly with the values of *x*, an observation that might be useful to study the incorporation of other chemical functions having well-defined and distinctive IR absorption bands. Also interesting were the gradual increase in the ν(CH) (aromatics) frequency from 3065 w, 3030 vw in **1** to 3086 m in **2**, $x = 2$, and the shift from 1270 to 1309 cm^{-1} for the ν-PO/PN band, both of which reflected the progressive oxidation of the polymer that becomes less electron rich with the nitration extent. The absence of intense bands in the 3400 cm^{-1} region showed that no water or acids were retained in the products.

Because of the low solubility in THF or CH_2Cl_2, the NMR spectra were best measured in DMSO as solvent in which perfectly transparent and concentrated viscous yellow solutions were formed. Conversely the starting **1** (very soluble in THF) was rather insoluble in DMSO, and the spectra made for comparison had to be measured overnight. The ^{31}P NMR spectra showed only a broad signal centered at a chemical shift that increased slightly with the incorporation of the NO_2 groups, varying from *ca.* −5.5 (the value for the starting polymer in this solvent) to −4.5 ppm, which corresponds to the totally nitrated polymer ($x = 2$). In the derivative with $x = 1$, the resolution was sufficient to reveal a shoulder near −5.5 ppm suggesting the presence of no nitrated biphenoxy units. Therefore, the nitration is not perfectly randomized and the chains of **2** most likely consist of mononitrated repeating units (the more abundant) alternated with a fraction of no nitrated and binitrated units. In fact, polymers **2** exhibited very high T_g's [in the range 169−236 °C by DSC] that varied almost linearly with the NO_2 contents (Figure 1), a behavior not corresponding to a family of strictly alternating random copolymers.[21] Furthermore both the shape of the signal of the ^{31}P NMR and the glass transition depended on the experimental conditions of the preparation. When the nitration (for $x = 1$) was carried out in nearly saturated H_2SO_4 solutions (ca. 2 g/5 mL) the product isolated had a conspicuous sharp peak at −5.5 in the ^{31}P NMR spectrum and a significantly lower glass transition temperature (171 °C), indicating the presence of long blocky segments of no nitrated units. (Nitration in highly diluted solutions was not feasible because the products could not be precipitated in water after the reaction.) A clear dependence of the ^{31}P NMR spectra and the T_g values with the structural homogeneity has been earlier observed in macromolecular substitution reactions leading to different random copolymers under different experimental conditions,[22] but this is the first time noted in a macromolecular derivatization leading to different distribution of repeating units depending on the concentration of the reagents.

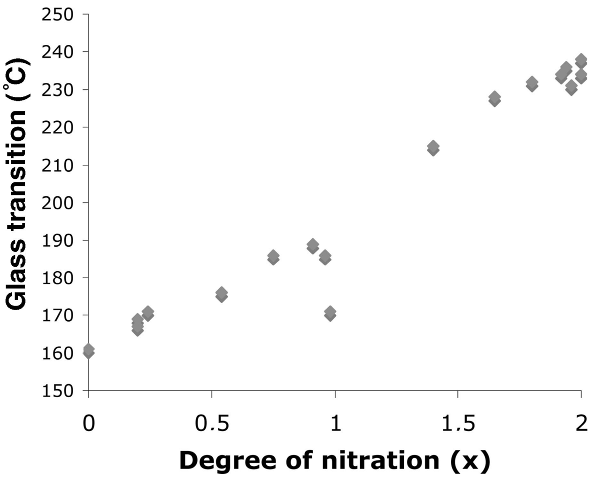


Figure 1. Glass transition temperature of **2** as a function of *x*. The lower value at *x* =1 corresponds to the material obtained in nearly saturated H_2SO_4 solution.

Because of the broadness of the signals, the ^1H spectra[23] were not very useful, but clearly showed the effects of the nitration on the dioxybiphenyl rings in the appearance of two broad unresolved multiplets centered near 7.8 and 6.8 ppm (the first being more intense) the relative intensity of which increased with the nitration extent. [As a reference, in DMSO, polymer **1** shows three broad signals centered at 7.4, 7.1 and 7.0 ppm, and the 5,5′-dinitro-2,2′-biphenol has signals at 8.3 q, 8.26 s, 7.02 d[24]]. Again the spectra of the partially nitrated products obtained in saturated or less concentrated solutions had different shapes suggesting the presence of blocky segments with non-nitrated units.

The ^{13}C NMR spectra were decisive to characterize the reaction products (see Figure 2) [as a reference, polymer **1** in DMSO shows broad signals centered at 148.7, 130, 129.3, 125.5 and 123.0]. The spectral peaks were assigned considering the dept-135 experiments, taking into account the intensity variations with the nitration extent, using an estimation of the chemical shifts based on the values corresponding to the *para* and *ortho* nitrophenols and the changes observed in the chemical shifts of the carbons in going from phenol HO−C_6H_4 (C_1 = 164, C_4 = 121) to the biphenoxyphosphazene polymeric units [$NP(O_2C_{12}H_8)$] (149, 125). Thus, the two intense peaks in the region (132−155) in the spectrum of the totally nitrated polymer (**2**, $x = 2$), which disappeared in the dept-135 experiments, could be unambiguously assigned to the C_2 (152 ppm) and C_5 (145 ppm) carbons of the 5,5′-NO_2 rings (in *para* nitrophenol the chemical shift of the C_5 carbon is 140 ppm). As there are an average of two NO_2 groups per biaryloxy unit, the two smaller peaks at 148 and 149 ppm are clearly indicating the presence of rings nitrated in other positions, and the most likely one is the 3,3′ (see later), a hypothesis supported by the six broad signals in the 135−115 ppm region (only a maximum of 4 is

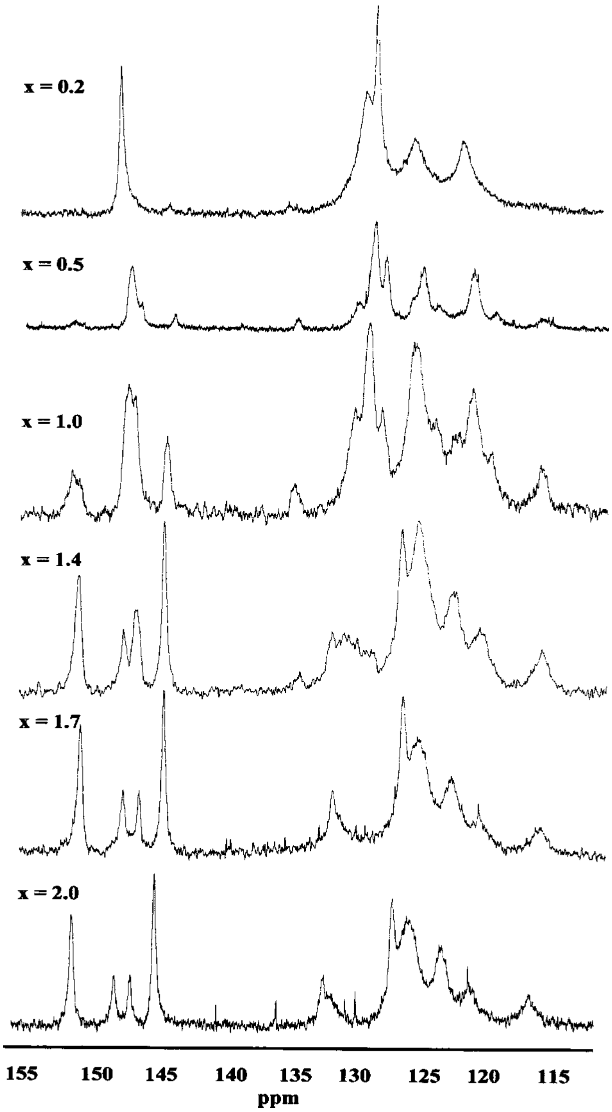


Figure 2. ^{13}C NMR spectra of **2** as a function of *x*.

expected for the pure 5,5′ dinitrated units). In fact, the two peaks at 148 and 149 ppm and that at 132 ppm agree well with what is expected for the C_2 carbons and C_3 carbon of 5,3′-bi nitrated rings (in *ortho* nitrophenol the chemical shift of the C_3 carbon is 135 ppm). Among the other signals only that at 127 ppm, that remained intense in the J-MOD experiment, could be unambiguously assigned to the C_1 carbons. The spectrum, therefore, clearly supports the nitration of the biphenoxy rings in both 5,5′ and 5,3′ positions, which is also consistent with the results observed in the nitration of the free 2,2′-dihydroxy-1,1′-biphenyl that gives a mixture of the 5,5′ and 5,3′ isomers.[25] Consequently, the chemical structure of **2**, $x = 2$, approaches that shown in Scheme 1 (a few rings nitrated in 3,3′ might be also possible).

In contrast with the case of the phenylphosphazene ring which, is nitrated in the expected[16] *meta* position,[26] like the nitrobenzene,[27] the nitration of **1** should be easier and might affect the *ortho* (3,3′) and *para* (5,5′) positions. However, it might be expected that the steric effects in the polymer chain should favor the latter. The distinct tendency of **1** to be nitrated in the 3 positions seems to indicate that in the sulfuric acid solutions the phosphazene chains adopt conformations where those positions are not so severely crowded. In fact, we observed that, even carrying out the reaction in the saturated solutions, the 3/5 nitration ratio remained almost invariable. In the case of $x = 1$, the ^{13}C NMR of the products obtained in the saturated solutions also evidenced (see above) the presence of the blocky no nitrated segments particularly by the high intensity exhibited by the peaks in the 149−147 ppm region corresponding to the C_2 carbons.

An attempt to improve the regioselectivity of the macromolecular nitration of **1** using $LiNO_3$ instead of HNO_3 (hoping that the interaction of the Li^+ cations with the weakly basic N atoms of the PN chain would hinder the approach of the NO_2^+ cations to the 3,3′ positions) was unsuccessful giving products with nearly the same 3/5 nitration ratio.

The thermal stability of **2** was studied by TGA in the absence of oxygen. The thermogravimetric curves showed a preliminary small loss of 0 to 4% below 300 °C due to some water content (also noted in the ^{1}H NMR spectra),[23] followed by a complex decomposition pattern that depended on the degree of nitration. Thus, the main loss, that for the lower nitrated **2** was centered near 450 °C, was split in two distinguishable steps, the first of which (in the interval 300−450 °C, centered near 380 °C) appeared better resolved as the NO_2 content increased (the parent phosphazene **1** undergoes a single loss of *ca.* 67% centered at 480 °C). The first fast decomposition at 380 °C is clearly related to the presence of the NO_2 groups, because in the case of the totally nitrated compound (**2**, $x = 2$) it was very sharp and corresponded to a weight loss of *ca.* 26%, close to the theoretical NO_2 content (28.8%). The total residues left after reaching the 800 °C were not completely stabilized. This was noted by prolonging the heating at 800 °C for 1/2 h that showed an additional loss that varied from *ca.* 5% ($x = 0.2$) to 13% ($x = 2$) leaving final residues that were lower as x increased. Therefore, all the TGA data indicates that the presence of the NO_2 groups in the biaryloxy units exerts a destabilizing effect on the polyphosphazene chains.

The reduction of the NO_2 groups present in **2** to form the NH_2 derivatives was attempted by several known methods. Thus, the catalytic hydrogenation[28] of **2** with H_2 (100−200 psi) in THF at 50 °C in the presence of PtO_2 for 15 h resulted only in a very small reduction (*ca.* 7%) of the relative intensity of the ν-NO_2 IR bands. No reaction was observed using sodium dithionite in refluxing water, a method that was used in the surface of nitro-aryloxy phosphazenes.[17] Only by using Lalancette's reagent ($NaBH_2S_3$) in refluxing THF for 29 h followed by aqueous HCl (12 h) and NaOH (24 h), as published for the nitrophenylphosphazenes,[16] the disappearance of the NO_2 absorptions in the IR spectrum was observed, giving the final product in less than 40% yield.

Conclusions

The polymer **1**, which is very soluble (2 g/5 mL) and perfectly stable in 98% sulfuric acid, can be nitrated in these solutions using HNO_3 or $LiNO_3$. The controlled nitration gave almost quantitatively the products $\{NP[O_2C_{12}H_{8-x}(NO_2)_x]\}_n$ (**2**) ($x = 0.2$ to 2) having 5,5′- and 5,3′-nitrated dioxy-biphenyl phosphorus rings, with a larger proportion of the 5,5′.

The variations of the glass transition temperatures with x indicated that the products were not perfectly alternating random, copolymers, having a distribution of differently nitrated repeating units, and that blocky segments of non-nitrated units are formed if the reaction is carried out in nearly saturated solutions.

The presence of the $-NO_2$ in the cyclic units exerts a destabilizing effect on the polyphosphazene chains.

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