Synthesis and pyrolysis of silicon and tin containing poly(2,2′-dioxy-1,1′-biphenoxy-phosphazenes)

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Abstract

The polyphosphazene $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(OC_6H_4Br)_2]_{0.5}\}_n$ (**1**) $[(O_2C_{12}H_8) = 2,2'$-dioxy-1,1′-biphenyl] that, as an strictly alternating copolymer, can be considered nearly as the homopolymer $[NP(O_2C_{12}H_8)NP(OC_6H_4Br)_2]_n$, was reacted first with ^tBuLi in THF at $-78\,°C$ to give the intermediate $[NP(O_2C_{12}H_8)NP(OC_6H_4Li)_2]_n$ (**2**) and subsequently with the chlorosilanes $SiMe_3Cl$ and $SiMe_2(C_6H_5)Cl$ or with the chlorostannane $SnMe_3Cl$, to obtain the new polyphosphazenes $\{(NP[O_2C_{12}H_8])_{0.5}[NP(OC_6H_4SiMe_3)_2]_{0.5-x}[NP(OC_6H_5)(OC_6H_4SiMe_3)]_x\}_n$ (**3a**) $(x = 0.15–0.5)$, $\{(NP[O_2C_{12}H_8])_{0.5}[N-(POC_6H_4SiMe_2Ph)_2]_{0.2}[NP(OC_6H_5)(OC_6H_4SiMe_2Ph)]_{0.3}\}_n$ (**3b**), and $\{(NP[O_2C_{12}H_8])_{0.5}[NP(OC_6H_5)(OC_6H_4SnMe_3)]_{0.5}\}_n$ (**4**), having a very regular distribution of the silicon or tin organometallic sites along the chains. The pyrolysis of the polymers in air at $800\,°C$ gave microcrystalline residues (characterized by IR, XRD, SEM and TEM-EDXA) consisting on phases of $SiO_2 \cdot P_2O_5 \cdot P_2O_{7.9} \cdot SiP_2O_7$, or, in the case of the tin derivative, almost pure SnP_2O_7. The results indicate that, while part of the Si content is lost during the pyrolysis, almost all the tin in the original polymer was incorporated to the final residue.

Keywords: Polyphosphazenes; Copolymers; Silicon; Tin; Pyrolysis

1. Introduction

Polyphosphazenes are a very important class of inorganic macromolecules [1]. Since the emerging of the organosilicon derivatives of phosphazenes [2], many types of silicon-containing polyphosphaz-

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enes have been reported [3–9], and several have been examined with respect to their permeability to different gases [10]. Various types of hybrid phosphazene–silicon materials have been synthesized [11], including polymeric networks, usually made by sol–gel techniques [12], and surface functionalized silica [13]. However, to our knowledge, no studies on the pyrolysis of polyphosphazenes with organosilicon pendant groups have been reported. Therefore, considering the interest in the pyrolytic studies of organometallic derivatives of polyphosphazenes [14] and

the possibility of formation of metal oxide nanoparticles [15] we have prepared new polyphosphazenes containing silicon and tin in order to characterize the products of their pyrolysis in air. Apart from some works on cyclophosphazenes containing MMe_3 groups (M = Si, Ge, Sn) [16], we found only one report in the literature describing the incorporation of $SnPh_3$ fragments to phosphazene high molecular weight polymers [17].

2. Experimental part

K_2CO_3 and Cs_2CO_3 were dried at 140 °C prior to use. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. The 2,2′-dihydroxybiphenyl $HO–C_6H_4–C_6H_4–OH$, the phenol $HO–C_6H_4–Br$, ${}^tBuLi$ (Aldrich), $Si(CH_3)_3Cl$, $Si(CH_3)_2PhCl$ and $Sn(CH_3)_3Cl$ (Merck) were used as purchased. The starting polymer $[NPCl_2]_n$ was prepared as described previously [18].

The IR spectra were recorded with a Perkin–Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200, AC-300 and Avance 300 instruments, using $CDCl_3$ as solvent unless otherwise stated. ^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. The ^{119}Sn and ^{27}Si NMR spectra were measured using as reference TMS or $SnMe_4$, respectively. Coupling constants are in Hertz. C, H, N analyses were performed with a Fissons CE instruments model AE-1108 microanalyzer. Bromine analyses were performed by Galbraith Laboratories. GPC were measured with a 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 300 differential scanning calorimeter equipped with a TA 1100 computer. Thermal gravimetric analyses 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 constant flow of nitrogen.

SEM images were made with a Philips EM 300 apparatus. Energy-dispersive X-ray analyses (EDXA) were performed using a Noran Instruments microprobe attached to a JEOL 5410 scanning electron microscope. TEM images were made on a JEOL SX 100 transmission electron microscope. The finely powdered samples were dispersed in n-hexane and dropped onto a conventional carbon-coated copper grid and dried with a lamp by 30 min. X-ray diffraction (XRD) was carried out at room temperature on a Siemens D-5000 diffractometer with θ–2θ geometry. The XRD data were collected using Cu-Kα radiation (40 kV and 30 mA) waves.

2.1. Synthesis of $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(OC_6H_4Br)_2]_{0.5}\}_n$ (1)

To a solution of $[NPCl_2]_n$ (3 g, 25.89 mmol) in THF (250 ml) were added 2-2′-$HOC_6H_4C_6H_4$-OH (2.41 g, 12.94 mmol) and K_2CO_3 (7.16 g, 25.89 mmol) and the mixture was refluxed for 14 h with vigorous mechanical stirring. Then, the phenol HOC_6H_4Br (13.4 g, 77.7 mmol) and Cs_2CO_3 (25.32 g, 77.7 mmol) was added, and refluxing was continued for 10 h. The mixture was poured into water (1 l) with stirring to give a solid that was washed with water and dried in air. The purification was performed by dissolving the product in THF (600 ml) to give a clear solution that was concentrated at reduced pressure until the formation of a viscous liquid that was poured portion-wise (Pasteur pipette) into water (1 l), followed by two further re-precipitations from THF/isopropyl–alcohol and THF/hexane. The final white material was dried 72 h in $vacuo$ at 50 °C. Yield: 6.7 g, 84%. Anal. Calc. for $NPO_2C_{12}H_8Br$ (309.06 g/mol): C, 46.6; H, 2.61; N, 4.53; Br, 25.9. Found: C, 45.6; H, 2.61; N, 4.66; Br, 22.7.

IR (KBr) cm^{-1}: $v = 3065w$ (v-CH-arom.), 2953m (v-CH-aliph.), 1603s, 1583s, 1482m (v-C=C-arom.), 1264vs (v-C–OP), 1245vs, 1193vs, br, 1160s (v-PN), 1095s (v-P–OC), 943vs, 924vs, br (δ-POC), 783s, 750m, 716m, 609w, 535s (other). $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = -43$ ppm, br [$NP(O_2C_{12}H_8)$], -21 ppm, br [$NP(OC_6H_4–Br)_2$]. ^1H NMR ($CDCl_3$): $\delta = 6.5$–7.4m, br ($C_{12}H_8$ and C_6H_4). $^{13}C\{H\}$ NMR ($CDCl_3$): $\delta = 117, 123, 129, 150$ ppm (OC_6H_4Br); 122sh, 125, 132, 148 ($O_2C_{12}H_8$).

GPC: M_w 950,000, $M_w/M_n = 2.1$.
TGA: -59% (479 °C). Residue at 800 °C: 41%.
DSC: $T_g = 72$ °C ($\Delta Cp = 0.19$ J/g K).

2.2. $\{(NP[O_2C_{12}H_8])_{0.5}[NP(OC_6H_4SiMe_3)_2]_{0.5-x}[NP(OC_6H_5)(OC_6H_4SiMe_3)]_x\}_n$ (3a)

Polymer (1) (3 g, 9.71 mmol, 9.71 mmol of Br) was dissolved in THF (300 ml). The solution was

cooled to $-78\,°C$ and ^{t}BuLi (12 ml, 1.7 M, 20.36 mmol) was added slowly, the mixture was stirred at this temperature for 1.5 h. Then, ClSi(CH$_3$)$_3$ (6 ml, 40,72 mmol) was added and the reaction mixture was stirred at $-78\,°C$ to room temperature for one night. The solution was concentrated *in vacuo* to a viscous liquid that was poured into water (100 ml) to form a white precipitate, which was washed with CH$_3$OH. The final white material was dried 24 h in vacuo at room temperature to give **3a** ($x = 0.13$). Yield 2.7 g, 90%.

Anal. Calc. for NPO$_2$C$_{14.5}$H$_{16}$Si$_{0.87}$ (292.75 g/mol): C, 59.9; H, 5.47; N, 4.78. Found: C, 57.7; H, 5.0; N, 4.83. Residual Br(0.07%).

IR (KBr) cm^{-1}: $v = 3066$w, 3026w (v-CH-arom.), 2954m, 2895w (v-CH, Si(Me)$_3$), 1590s, 1569vw, 1498m, 1477m (v-C=C-arom.), 1260vs (v-C–OP), 1248vs, 1199vs, br, 1170vs (v-PN), 1109s, 1096s (v-P–OC), 950–940vs, br (δ-POC), 830–850s, br, 784s, 751m, 716m, 608w, 535s (other).

^{31}P{H} NMR (CDCl$_3$): $\delta = -5{,}6$ ppm, br [NP(O$_2$C$_{12}$H$_8$)], -21.2 ppm, br [NP(OC$_6$H$_4$–)$_2$].

^{1}H NMR (CD$_2$Cl$_2$): $\delta = 6.5–7.3$m, br (C$_{12}$H$_8$, C$_6$H$_4$ and C$_6$H$_5$), 0.03m, br (CH$_3$). Intensity ratio Me(Si)/(aromatics) = 0.96.

^{13}C{H} NMR (CDCl$_3$): $\delta = 120$, 123, 129, 152 ppm (OC$_6$H$_4$Si); 123sh, 125, 134, 149 (O$_2$C$_{12}$H$_8$), 1.08 ppm (CH$_3$).

^{28}Si NMR (CDCl$_3$): $\delta = -4.8$ ppm.

GPC: M_w 740,000, $M_w/M_n = 2.2$.

TGA: -8% (229 °C), overlapped with -65% (460 °C). Residue at 800 °C: 27%.

DSC: $T_g = 78\,°C$ ($\Delta Cp = 0.2$ J/g K).

In other reactions carried out similarly the resulting products **3a** had values between $x = 0.13$ and 0.48, as measured by the agreement between the intensity ratios Me(Si)/(aromatics) (0.96–0.55, respectively) and the analytical C, H, N data. For the lower silicon containing product ($x = 0.48$), the data calcd.(found) was: C, 60.9(58.6), H, 4.92(4.57), N, 5.22(5.10). The M_w's were around 700.000 with IPD near 3, and T_g values were in the range 78 °C ($x = 0.13$) to 76 ($x = 0.48$). In all cases the TGA thermograms showed a first small loss (ca. 6%) centred near 230 °C and overlapped with sharp main loss (ca. 60%) centred at 460 °C, with final residues at 800 °C in the proximities of 23–27%. Only the less Si containing product had a lower residue: TGA: -3% (116 °C), -40% (373 °C), -42 (735 °C). Residue at 800 °C: 15%.

2.3. {(NP[O$_2$C$_{12}$H$_8$])$_{0.5}$[NP(OC$_6$H$_4$SiMe$_2$Ph)$_2$]$_{0.2}$- [NP(OC$_6$H$_5$)(OC$_6$H$_4$SiMe$_2$Ph)]$_{0.3}$}$_n$ (3b)

This synthesis was carried out in an analogous manner to **3a**, using polymer (**1**) (0.309 g, 0, 97 mmol, 0.97 mmol of Br), 50 ml THF, ^{t}BuLi (1.2 ml, 1.7 M, 2.04 mmol) and Si(CH$_3$)$_2$PhCl (0.69, 4.0 mmol). Polymer **3b** resulted as a white material. Yield 0.24 g, 80%.

Anal. Calc. for NPO$_2$C$_{17.5}$H$_{16}$Si$_{0.7}$ (323.8 g/mol): C, 65.2; H, 4.94; N, 4.32. Found: C, 62.4; H, 4.25; N, 4.14.

IR (KBr) cm^{-1}: $v = 3067$w, 3020w (v-CH-arom.), 2954m, 2895w (v-CH, Si(Me)$_3$), 1589s, 1499m, 1477m (v-C=C-arom.), 1247vs (v-C–OP), 1193vs, br, 1170s (v-PN), 1109s, 1095s (v-P–OC), 950–940vs, br (δ-POC), 825m, 813s, 774s, 750s, 716m, 698m, 658w, 607m, 534s (other).

^{31}P{H} NMR (CDCl$_3$): $\delta = -5.5$ ppm, br [NP(O$_2$C$_{12}$H$_8$)], -21 ppm, br [NP(OC$_6$H$_4$–)$_2$].

^{1}H NMR (CD$_2$Cl$_2$): $\delta = 8.5–6$m, br (C$_{12}$H$_8$, C$_6$H$_4$ and C$_6$H$_5$), 0.3 br (CH$_3$). Intensity ratio Me(Si)/(aromatics) = 0.36.

GPC: M_w 840,000, $M_w/M_n = 3.0$.

TGA: -10% (290 °C) overlapped with -54% (470 °C) and -9 (758 °C). Residue at 800 °C: 27%.

DSC: $T_g = 62\,°C$ ($\Delta Cp = 0.21$ J/g K).

2.4. {(NP[O$_2$C$_{12}$H$_8$])$_{0.5}$[NP(OC$_6$H$_5$)(OC$_6$H$_4$- SnMe$_3$)]$_{0.5}$}$_n$ (4)

This synthesis was carried out in an analogous manner to **3a**, using polymer **1** (0.309 g, 0, 97 mmol, 0.97 mmol of Br), 50 ml THF, ^{t}BuLi (1.2 ml, 1.7 M, 2.04 mmol) and Sn(CH$_3$)$_3$Cl (0.797 g, 4.0 mmol). Polymer 4 resulted as a white material. Yield 0.31 g, 83%.

Anal. Calc. for NPO$_2$C$_{13.5}$H$_{13}$Sn$_{0.5}$ (311.5 g/mol): C, 52.0; H, 4.17; N, 4.49. Found: C, 49.2; H, 3.95; N, 4.16.

IR (KBr) cm^{-1}: $v = 3061$w, 3026d (v-CH-arom.), 2976w, 2912w [v-CH, Sn(Me)$_3$], 1581m, 1491m, 1477m (v-C=C-arom.), 1247s (v-C–OP), 1196vs, br, 1169vs (v-PN), 1096s, 1070m, (v-P–OC), 944s. br (δ-POC), 822m, br, 783s, 751s, 716m, 608m, 529s (other).

^{31}P{H} NMR (CDCl$_3$): $\delta = -5.6$ ppm, br [NP(O$_2$C$_{12}$H$_8$)], -22 ppm, br [NP(OC$_6$H$_4$)$_2$].

^{1}H NMR (CD$_2$Cl$_2$): $\delta = 6.5–7.3$m with a maximun at 6.9, br (C$_{12}$H$_8$, C$_6$H$_5$ and C$_6$H$_4$), 0.13m, br (CH$_3$, $J^2_{HSn} = 50$ Hz). Intensity ratio Me(Si)/(aromatics) = 0.55.

$^{13}C\{H\}$ NMR (CDCl$_3$): δ ppm $= 152$, 149, 136, 129, 128, 125, 124, 123, 122, 121 (O$_2$C$_{12}$H$_8$, OC$_6$H$_5$ and OC$_6$H$_4$), -9.5 ppm (SnCH$_3$, $J^1_{CSn} = 340$ Hz).

^{119}Sn NMR: -27 ppm.

GPC: M_w 1400,000, $M_w/M_n = 3.5$.

TGA: -2% (107 °C) (water retained), -20% (256 °C), -31% (442 °C), -16% (760 °C). Final residue at 800 °C: 31%.

DSC: $T_g = 87$ °C ($\Delta Cp = 0.1$ J/g K).

2.5. Pyrolysis of the polymers

The pyrolytic experiments were carried out by placing weighed samples (0.05–0.15 g) of the polymer into aluminium oxide boats, which were placed in a tubular furnace under an air flow. The polymer samples were heated at a rate of 10 °C min^{-1} from room temperature up to 800 °C under a constant air flow of 120 ml/min. The yields were in the range of 15–20% (**3a**), 5% (**3b**) and 33% (**4**).

3. Results and discussion

One of the various methods to prepare organophosphazene–organosilicon polymers [6] is based on the reaction of organosilane chlorides with lithioaryloxy phosphazenes, the latter being formed by direct lithiation of the corresponding bromophenoxy phosphazenes with buthyl lithium, as first reported [19] in 1979. Therefore, the synthesis of the new polymers **3** and **4** was carried out in as shown in Scheme 1.

First, following the method described earlier [20] the chlorine containing phosphazene {[NP(O$_2$-C$_{10}$H$_8$)]$_{0.5}$[NPCl$_2$]$_{0.5}$}$_n$ was reacted in refluxing THF with *p*-bromophenol and caesium carbonate to give the new copolymer {[NP(O$_2$C$_{10}$H$_8$)]$_{0.5}$-[NP(OC$_6$H$_4$Br)$_2$]$_{0.5}$}$_n$ (**1**) isolated as a white solid in very high yield (see Scheme 1). The M_w (GPC) was of de order of 10^6.

The glass transition temperature found for **1** (72 °C), and those corresponding to the similar polymer with 0.65 [NP(OC$_6$H$_4$Br)$_2$] units (55 °C) [20] and to the homopolymers [NP(O$_2$C$_{10}$H$_8$)]$_n$ (161 °C) [20] and [NP(OC$_6$H$_4$Br)$_2$] (8 °C) [21], indicated that, as observed for other copolymes of this type [22], the chains of **1** are close to the strict alternation of the two different NP units. Therefore it can be considered nearly as an homopolymer of composition {[NP(O$_2$C$_{10}$H$_8$)NP(OC$_6$H$_4$Br)$_2$]$_n$, with a regular distribution of the bromophenoxy groups along the chains.
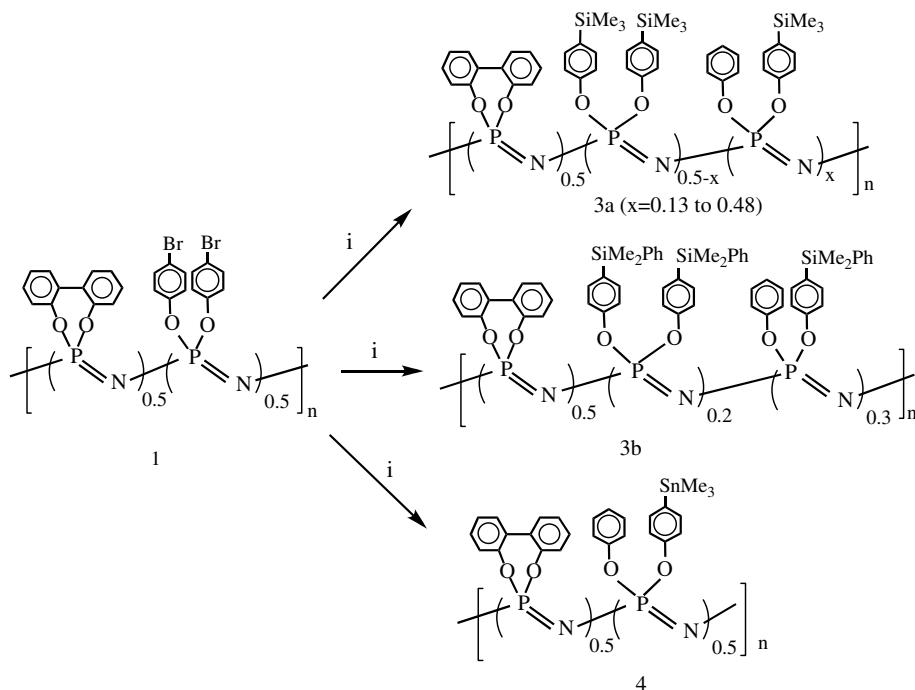
Scheme 1. ^{t}BuLi (3.2 equiv.) THF/-78 °C followed by SiMe$_3$Cl or SiMe$_2$PhCl or SnMe$_3$Cl.

As observed with previously reported binaphth-oxyphosphazenes [9], the treatment of (1) with ^{t}BuLi (2.1 eq per eq of Br) in THF at $-78\,°C$ yielded the totally lithiated derivative $[NP(O_2C_{12}H_8)NP(OC_6H_4Li)_2]_n$ (2) that was reacted in situ with $SiMe_3Cl$ (2 eqs per eq ^{t}BuLi used in the first step) to give the silicon-containing polymers with composition $\{(NP[O_2C_{12}H_8])_{0.5}[NP-(OC_6H_4SiMe_3)_2]_{0.5-x}[NP(OC_6H_5)(OC_6H_4SiMe_3)]_x\}_n$ (3a) (Scheme 1), isolated as white solids in ca. 90% yields. Various repeated experiments increasing the equivalents of ^{t}BuLi from 2 to 4 per Br, or increasing the ratio $SiMe_3Cl/^tBuLi$ from 2.1 to 3.2, confirmed that the silicon incorporated to the polymer was always below the maximum expected ($x = 0$). The values varied from the more frequent 87% (products with $x = 0.13$) and the minimum observed 52% ($x = 0.48$). The incomplete silylation is typical in this type of reactions in phosphazenes [8,10b] and has been attributed to the moist sensitivity to trace amounts of water, or, more interestingly, to the lower solubility of the highly lithiated products [8]. In fact, we checked that the residual bromine in 3a was almost negligible (0.07%) demonstrating that the lithiation of 1 was complete. Therefore, although copolymers like 1 tend to adopt extended conformations in THF (random coil) [23], the higher ionic character of the lithiated chains [8] makes the aggregation of polymer 2 more likely diminishing the degree of accessibility of the $SiMe_3Cl$ reagents and preventing a complete silylation, specially at low temperatures. Steric factors are also very likely to be operative in this type of reactions, as previously observed [10b].

The M_w, that ranged from 0.6 to 0.7×10^6 by GPC, were similar to that of the precursor 1. In fact, the slightly lower values observed should be considered with caution because the possibility of inter-chain aggregation may cause some uncertainty in the M_w of polyphosphazenes as measured by GPC [24]. The glass transition temperatures were very similar (in the range 75–$80\,°C$) showing that the replacement of Br by the group $SiMe_3$ has little effect. As expected [10b], however, a very slight increase in the T_g was observed as the silicon content in the polymer increased.

All the analytical and spectroscopic data (Section 2) supported the composition and structure of 3a. The %C found was reasonably good for polymeric materials of this type, and the slightly lower values could be explained by the incomplete combustion, as demonstrated by the results of the pyrolytic studies (see below).

As the lithiation of 1 was complete (see above) the non-silicon containing sites originated after the silylation step (see above) should be OC_6H_5 groups, and if, as expected, the $SiMe_3$/Li substitution occurred in a random manner, the fraction of $[NP(OC_6H_6)_2]$ groups should be almost negligible, specially when the replacement of Br by Si is over 50%. Therefore, the disposition of the $SiMe_3$ groups along the chains of 3a is highly regular approaching the idealized structure shown in Fig. 1 for $x = 0.5$.

The IR spectrum evidenced the incorporation of the $SiMe_3$ fragment to the polymeric chains by the strong v(CH) aliphatic bands typical of this group [25] at $2954\,cm^{-1}$ (strong) and $2895\,cm^{-1}$ (weak), the intensity of which (relative to the CH aromatic weak bands of the biphenoxy group at $3066\,cm^{-1}$) increased with the silicon content. The IR spectra also showed one sharp band at $1109\,cm^{-1}$ (not present in the precursor 1) which were more intense in the polymers with higher silicon contents, and that might be attributed to the phenyl-Si group [25, p. 338]. Other broad signals between 826 and $850\,cm^{-1}$ could be assigned to the out of plane CH deformations of the para-substituted rings O–C_6H_4–$SiMe_3$ [25, p. 78].

The ^{31}P NMR showed the expected two broad signals of equal intensity, one at $-5.6\,ppm$ for the $[NP(O_2C_{12}H_8)]$ units and other, slightly broader, at $-21\,ppm$ for the $[NP(OC_6H_5)(OC_6H_4SiMe_3)]$ and $[NP(OC_6H_4SiMe_3)_2]$ units. The sharp singlet in the ^{27}Si NMR spectrum at $-4.8\,ppm$ confirmed the presence on the $SiMe_3$ group in only one chemical environment.

The relative intensities of the signals corresponding to the $SiMe_3$ (0.05 ppm) and to the aromatic protons at (6.5–7.3 ppm) in the ^1H NMR spectra, agreed perfectly with the proposed formulas.

Analogously to the formation of 3a, the reaction of 1 first with ^{t}BuLi at $-78\,°C$ followed by the addition of $SiMe_2PhCl$ gave the polymer of composition
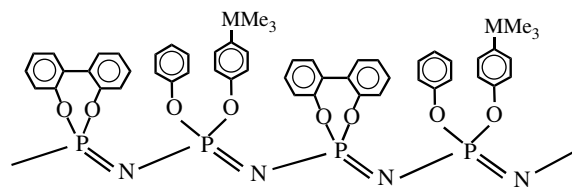
Fig. 1. Distribution of units along the chains in 3a (M = Si) for $x = 0.5$ and 4 (M = Sn).

{(NP[O_2C_12H_8])_{0.5}][NP(OC_6H_4SiMe_2Ph)_2]_{0.2}[NP(O-C_6H_5)(OC_6H_4SiMe_2Ph)]_{0.3}}_n (**3b**), (Scheme 1) that was similarly characterized (attempts made with SiMePh_2 gave only insoluble not well characterized products with little Si-contents).

The M_w of **3b** was also of the order of 10^6, and the T_g (62 °C) was lower than the polymer **3a** with the same Si content ($x = 0.3$). This might be surprising because, in principle, the change of a SiMe_3 group by the more voluminous SiMe_2Ph should contribute positively to the T_g. However, the same effect has been already observed in other type of silicon-containing polyphosphazenes [10b].

In the case of **3b**, the IR spectrum showed a less intense signal for the v-CH stretching modes of the Si–CH_3 group (2954 cm^{-1}), and a sharper medium band at 813 cm^{-1}, for the out of plane CH deformations of the *para*-substituted O–C_6H_4–SiMe_2Ph group.

The TGA thermograms of the polymers **3a** and **3b** showed a first small loss (ca. 6–9%) centred near 230 °C, partly overlapped with the main sharp loss (ca. 60%) centred near 460 °C due to the depolymerization and volatilization of organic decomposition products [26], with final residues at 800 °C were in the range of 25%. Only the **3a** derivative with less Si content had a lower residue (15%). Considering the precedent [17] of the use of SnPh_3Cl, we reacted the lithiated derivative of **1**, with SnMe_3Cl to give the soluble tin-containing polyphosphazene with formula {(NP[O_2C_12H_8])_{0.5}] [NP(O-C_6H_5)(OC_6H_4SnMe_3)]_{0.5}}_n (**4**). All the analytical and spectroscopic data supported the formulation (see Section 2). The regular chain structure is that of the analogous **3a** with $x = 0.5$ (Fig. 1). The M_w (1.4×10^6) was apparently higher but probably due to the effect of aggregations. As expected, the T_g (87 °C) was higher than the analogous silicon polymer **3a** with $x = 0.5$. As expected, the final residue at 800 °C in the TGA thermogram (31%) was higher than that found for the analogous Si-polymer **3a**. The IR spectrum showed that the v(CH) stretching frequency of the SnMe_3 group (2976 cm^{-1}) is higher than that of the silicon analogue, and, although no intense IR bands were found at 1109 cm^{-1}, a weak-medium band at 822 cm^{-1} could be assigned to the CH deformations of the *para*-substituted O–C_6H_4–SnMe_3 group. Only one sharp signal at −27 ppm was observed in the ^{119}Sn NMR spectrum, and the ^{13}C NMR spectrum showed the carbons of the methyl groups (−9.52 ppm) with the expected ^{119}Sn satellites

($^1J_{SnC} = 340$ Hz). The satellites corresponding to the CH_3 singlet in the broad ^{1}H NMR spectrum were observed as two shoulders separated by 50 Hz, indicating that the ^{2}JSn–C–H coupling constant is also in the expected range [27].

The pyrolysis in air of the silicon and tin-containing polyphosphazenes was studied at 800 °C. The resulting grey pyrolytic residues were characterized by SEM-EDAX, IR, TEM and XRD. The pyrolytic yields were higher for the tin derivative **4** (33%) than for the silicon polymers (15–20%). Those values were consistent with the residues measured by TGA experiments to 800 °C in the presence of air, that were lower than those obtained under N_2.

The SEM images of the residues (Fig. 2) showed fused granular microstructures, more fibrous in appearance in the case of the tin derivative **4** (Fig. 2b).

The X-ray powder diffraction (XRD) pattern of the pyrolytic products corresponding to the Si polymers with different values of x were very similar
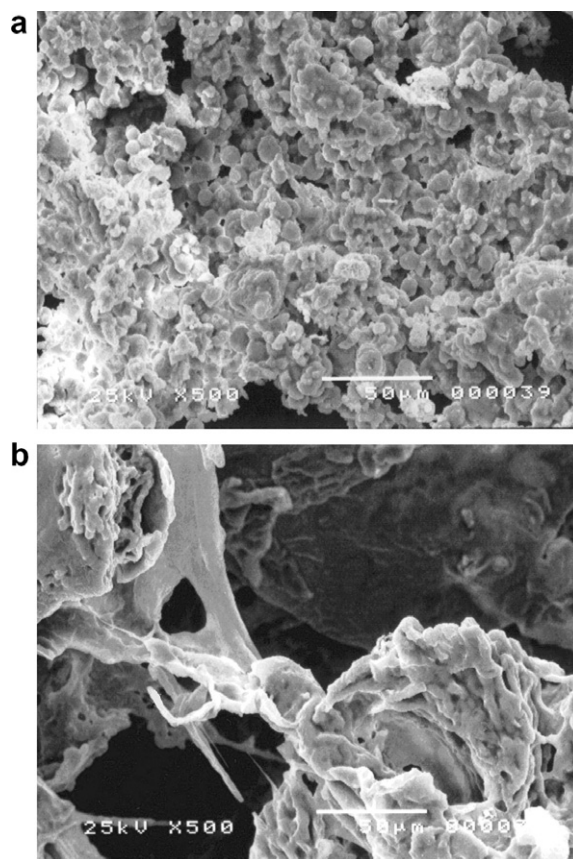

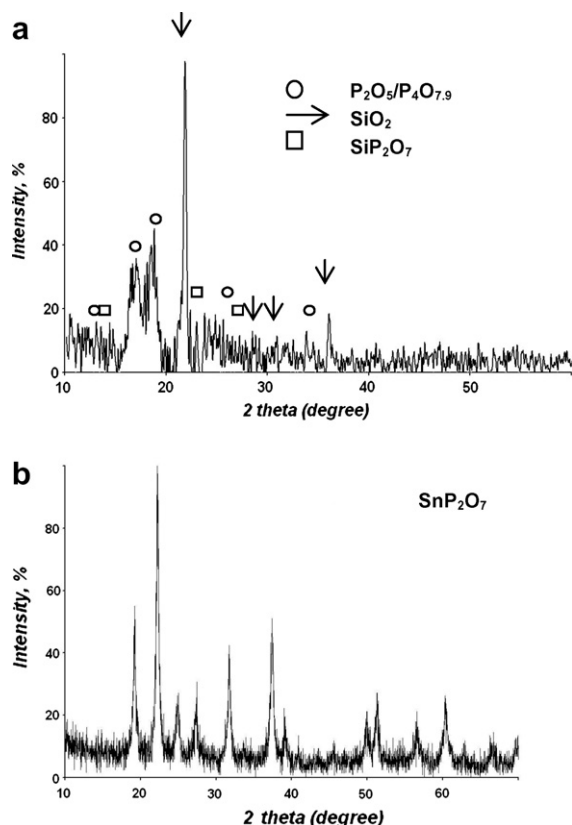Fig. 2. SEM images for the pyrolytic products. (a) **3a** ($x = 0.48$), (b) for **4**.

Fig. 3. XRD patterns of the pyrolytic residues. (a) **3a** ($x = 0.13$), (b) **4**.

(Fig. 3a shows that for polymer **3a**, $x = 0.48$). Sharp reflections corresponding to SiO_2 (cristobalite) (JCPDS card No. 01-082-0512) and broad multicomponent signals that can be assigned to phosphorous oxides P_2O_5–$P_4O_{7.9}$ (JCPDS card No. 01-085-1120 and 01-071-2124) were observed. Only very weak signals of silicon phosphate SiP_2O_7 (01-082-1061) could be found. By contrast, the XRD pattern of the pyrolysis product from **4** (see Fig. 3b) displayed only the typical peaks corresponding to tin diphosphate SnP_2O_7 (JCPDS card No. 00-029 1352) and no peaks for SnO_2 were noted.

Consistently, the IR spectra of the pyrolytic residues of the silicon polymers **3a** showed absorptions at 1180–1050vs, br cm^{-1}, 800–680w cm^{-1}, and 490s, br cm^{-1}. The IR spectrum of the cristobalite [28] shows a strong broad signal centred at 1100 cm^{-1}, a weak one around 800 cm^{-1}, and a strong one at ca. 450 cm^{-1}. Therefore, the absorptions in the 1100–1180 cm^{-1} region of the more intense and broad band should correspond to the PO vibrations [29].

Also in agreement with the XRD data, the IR spectrum of the pyrolytic products of **4** (strong broad absorptions centred at 1170vs, 1014m, 740w, 538m cm^{-1}) was identical to that reported [30] for SnP_2O_7.

The energy-dispersive X-ray analyses (EDXA) showed the presence of the expected elements and indicated the presence of traces of C, showing that not all this element is lost in the pyrolysis and explaining that the analytical %C found was slightly lower than the theoretical value.

On the other hand, the Si/P atomic ratio measured in the pyrolytic residues of polymers **3a** were reasonable homogeneous within different sample points, and the overall values were in the range from 0.5(for $x = 0.13$) to 0.3($x = 0.48$), i.e, lower than in the starting polymer although higher as the amount of Si increases. This indicates that some silicon is lost in the volatiles formed during the pyrolysis. However, in the case of **4**, the total percentage of tin in the starting material (measured from the 33% pyrolytic residue multiplied by its 62.7% Sn content) was 20.7, a value reasonably close to the theoretical 19.1%. This and the overall atomic ratio Sn/P = 0.6 (theoretical 0.5) suggested that no significant amounts of tin ware lost during the pyrolysis.

It is noteworthy that the formation of a protecting layer of phosphates during the reaction of polyphosphazenes with oxygen may be of interest in the design of atomic oxygen resistant materials [31].

4. Conclusions

The phosphazene random copolymer $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(OC_6H_4Br)_2]_{0.5}\}_n$ can be considered nearly as the homopolymer $[NP(O_2C_{12}H_8)NP(OC_6H_4Br)_2]_n$. It can be lithiated to give the reactive intermediate $[NP(O_2C_{12}H_8)NP(OC_6H_4Li)_2]_n$, that is a useful precursor for the synthesis of silicon or tin-containing polyphosphazenes with a very regular distribution of the silicon or tin organometallic sites along the chains. The pyrolysis under air at high temperatures of those polymers gave Si and Sn containing materials consisting on phases of $SiO_2 \cdot P_2O_5 \cdot P_2O_{7.9} \cdot SiP_2O_7$, or, in the case of the tin derivative, almost pure SnP_2O_7. While part of the Si content is lost during the pyrolysis, almost all the tin is incorporated to the final residues.

Acknowledgements

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