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Chlorination, Iodination, and Silylation of Poly(2,2′-dioxy-1,1′-biphenylphosphazene). New Halogenated Polyphosphazenes with Sterically Hindered Reactivity

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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] with $[PO_2C_{12}H_8]$ cycles in the repeating units reacts slowly with chlorine in concentrated sulfuric acid to give the 5,5′-chlorinated $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7Cl)]_x\}_n$ (**2**) ($x = 0.2-1$), with limiting oxygen index (LOI) in the interval 26−33 (estimated from the TGA residues), corresponding to potential self-extinguishing flame retardants. The reaction of **1** with $[Ipy_2]BF_4$ in CH_2Cl_2 in the presence of CF_3SO_3H gave the 5,5′-iodinated $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7I)]_x\}_n$ (**3**) ($x = 0.2-1$) which, in contrast, are thermally unstable, leaving almost no TGA residues. The potential of **2** and **3** as precursors for the chemical derivation of **1** was assessed by the silylation method (reaction with $LiBu^t$ at −78 °C followed by addition of $ClSiMe_3$ and a complete characterization of the resulting trimethylsilyl derivatives). The isolation of polymers $\{[NP(O_2C_{12}H_8)]_{0.65}[NP(O_2C_{12}H_7Cl)]_{0.15}[NP(O_2C_{12}H_7SiMe_3)]_{0.2}\}_n$ (**4**) and $\{[NP(O_2C_{12}H_8)]_{0.8}[NP(O_2C_{12}H_7SiMe_3)]_{0.2}\}_n$ (**5**) demonstrated that the lithiation was 40−50% efficient with the chlorine derivatives and approached 100% with the iodine analogues. The silylation of the available Li sites was less effective with the higher lithiated polymers and always below the levels usually observed. The reactivity of polyphosphazenes with 2,2′-dioxy-1,1′-biphenylphosphorus repeating units is therefore limited by steric and conformational effects reinforced by the proximity of the reaction centers to the main chain.

Introduction

The synthesis, properties, and applications of polyphosphazenes have been thoroughly reviewed.[1,2] A very important area of research concerns the incorporation of useful chemical functions by performing direct reactions on pendant groups attached to the main chain or to a polymer surface.[3−6] In practice, the success of this very versatile route to functionalized materials with predetermined properties depends on many factors, including *the degree of accessibility of the reactive centers to the incoming reagents* largely dictated by the behavior of the polymers in solution. In fact, because of the numerous steric and electronic effects involved at the polymer level, the regiochemistry of the reactions is frequently out of the experimentalist control. It has been shown that in processes such as the sulfonation the chemical modification of a precursor polymer may introduce significant irregularities in the products, in which case the substitution reaction from a chlorophosphazene and a nucleophile already carrying the desired chemical function may be more efficient.[7] An example is the incorporation of PPh_2 groups to aryloxyphosphazenes using directly $HO-C_6H_4-PPh_2$ in the presence of cesium carbonate.[8] It is clear however that, under the appropriate conditions, the direct route might be more desirable because it permits the syntheses of many different materials from a single starting polymer. All this makes the chemical reactivity of polyphosphazenes a very relevant subject. So far, much of the work has been concentrated on reactions of phosphazenes with aryloxide groups $-N{=}P-OCH_6H_4-X$ (X = H, halogen, NO_2, NH_2, CH_3, OCH_3, CN, CHO, COOR, etc.).[9] Other examples of chemical modification of pendant groups as a route to functionalized polyphosphazenes can be found in the literature.[10] However, only a few attempts have been made to halogenate aromatic substituents in polyphosphazenes, such as the bromination with *N*-bromosuccinimide of methylphenoxy groups that gave the bromomethyl derivatives without affecting the arene ring.[3b] In fact, the synthesis of halophenoxy derivatives has been achieved by introducing halophenoxide nucleophiles by macromolecular substitution.[11]

In earlier works[12] we reported the preparation of the soluble polyphosphazene $[NP(O_2C_{12}H_8)]_n$ (**1**), with averaged M_w of the order of 10^6 (Scheme 1). Several studies showed that this new type of polymer behaved as random coils in solution and that could be thermally degraded to distributions of lower average M_w.[13] So far, however, the study of its chemical reactivity has been limited to the acidic degradation[14] and nitration with HNO_3 in concentrated sulfuric acid.[15] Therefore, we have investigated the halogenation of **1** and examined the possibilities of the products as sources for other functionalized polyphosphazenes. The results have led to a new type of regular chlorinated polyphosphazenes that may be candidates for self-extinguishing flame retardants and to new iodo-derivatives that were less thermally stable leaving no TGA residues. Evidences have been found to support the idea that the reactivity of these polymers toward halogenation and further chemical derivation may be hindered by conformational changes and the proximity of the reaction centers to the main chain.

Results and Discussion

Bubbling chlorine gas into a dichoromethane solution of **1** at room temperature for several hours lead to the slow chlorination

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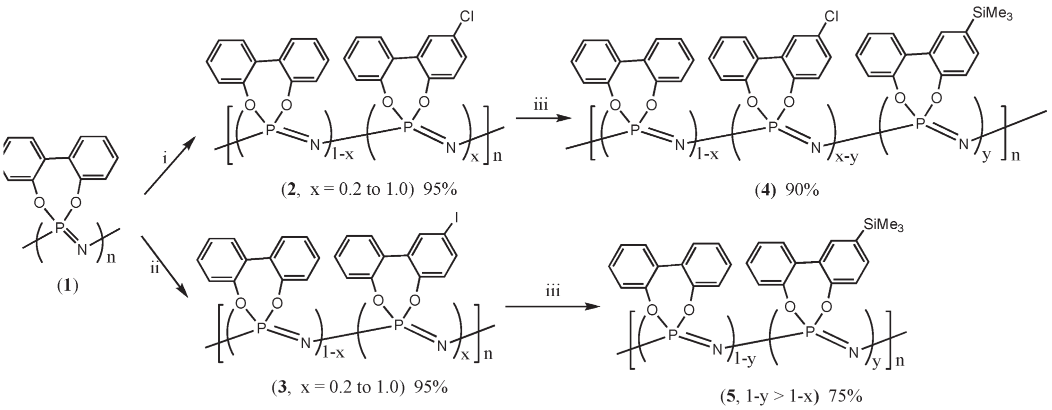
Scheme 1. [a]



[a] Reagents and conditions: (i) Cl_2 /H_2SO_4; (ii) [Ipy_2]BF_4/HSO_3CF_3 in Cl_2CH_2; (iii) 1, LiBu^t THF, −78 °C; 2, $ClSiMe_3$. The % yields are approximate averaged for all the compounds.

of the biphenoxy rings, as clearly revealed by the new bands at 824 and 649 cm^{-1} in the IR of the isolated products and by a new signal at 147 ppm in the ^{13}C NMR spectra attributable to the C2 of the aromatic rings (see later). However, the ^{31}P NMR spectra showed an unexpected broad signal at −19 ppm (5% relative to the main signal at −6 ppm), revealing a secondary reaction. Although it could not be demonstrated, this was probably originated by the opening of some of the dioxybiphenylphosphorus rings. However, it could be avoided by effecting the chlorination in concentrated sulfuric acid (98%) as solvent. The reaction was even slower but the chlorinated products {[NP($O_2C_{12}H_8$)]$_{1-x}$[NP($O_2C_{12}H_7Cl$)$_x$]}$_n$ (**2**) with x in the range 0.2−1.0 (without reaching the upper limit) could be isolated as white solids in ca. 95% yields (Scheme 1). Very small amounts of a yellow oil (better observed in the larger scale experiments) consisting of cyclic and oligomeric materials with chlorinated biphenoxyphosphazene units were separated during the isolation and purification of the products. This revealed a negligible chemical degradation during the reaction. The M_w of **2** (in the range 10^5) were consistent with the chain-length reduction expected for **1** after several hours in sulfuric acid.[14]

The actual degree of chlorination reached was always below $x = 1$ and depended on several experimental factors. In less concentrated solutions [1 g of **1** in 40 mL of H_2SO_4] bubbling chlorine (ca. 120 bubbles/min) for 15 min followed by stirring for 1 or 15 h gave $x = 0.4$ or 0.7, respectively. Bubbling for 1 h followed by stirring for 0 or 15 h gave $x = 0.5$ or 1. Rechlorination of derivatives with x close to 1 for 2 h followed by stirring overnight increased the chlorine content only slightly. All these observations lead to the large scale preparation of **2** with $x = 0.3$ (see Experimental Section). Considering the intrinsic basicity of those polymers,[14] in order to remove any possible traces of H_2SO_4 retained in the solids (specially those intended for the lithiation experiments), the material was further reprecipitated from THF/aqueous NaOH and dried until no significant amounts of solvents or humidity were present.

The characterization was accomplished by analytical and spectroscopic data. Repeated elemental analyses with purified and repurified samples were consistent with $x = 0.3 \pm 0.05$ although, as usually observed in this kind of phosphazene, the carbon contents were slightly below the calculated values. This fact is probably related to the difficulty of complete combustion (see later).

The IR spectra of **2** (Experimental Section and Supporting Information) were almost equal to that of **1** with only two extra bands located at 823 and 648 cm^{-1}. The first falls well in the range of the out-of-plane CH deformations modes of the of arene rings[16a] and proved the presence of the new substituted dioxybiphenyls. The band at 648 cm^{-1} is in the low limit of the range for a ν(C_{arom}−Cl) vibration.[16b] Further proof came from a comparison of the spectra that evidenced a nearly proportional increase of the intensity of the band at 648 cm^{-1} (measured with respect to that at 717 cm^{-1}, i.e., the ratio I_{648}/I_{717}) with the degree of chlorination given by x.

The ^{13}C NMR spectra (Experimental Section and Supporting Information) showed that most chlorine atoms were in the 5-positions with only a very small fraction in the 3-positions. Thus, a tentative assignment of the peaks (consistent with the values known for 5- and 3-chlorophenols, the relative intensities of the signals as a function of x, and the dept 3 and 6 jmod routines to differentiate C and CH carbons) indicated that the more intense peaks at 149 (C2), 129.2, 128.8 (C1, C6, C4), 125 (C5), and 123 ppm (C3), all in perfect coincidence with those of the homopolymer **1**, corresponded to the ($O_2C_{12}H_8$)P rings and the weaker signals at 147 (C2), 131 (C1), 128 (C5) and 124 ppm (C3) to the 5-chlorinated units. It is known that in chlorinated bisphenol-based phosphoramidites having ($O_2C_{12}H_4Cl_4$)P−NR_2 groups with Cl atoms in the 5,5′- and 3,3′-positions the C2 carbons appear as a doublet at 147 ppm, the C1 as a doublet at 132 ppm, the C5 is among the numerous peaks between 129 and 126 ppm, and the C3 carbon as a doublet at 127.9 ppm.[17] The appearance of another very weak peak at 145 ppm in the spectra of **2** was attributed to C2 carbons of a (very small) fraction of rings with Cl atoms in the 3-positions. The ^{13}C NMR spectra of polymers **2** with higher chlorine contents also showed discernible though exceedingly weak peaks at 150 and 134 ppm (not appearing in the products chlorinated in dichoromethane as solvent) that were consistent with the presence of some $-SO_3$ groups. This was also confirmed by the elemental analyses that revealed a small %S (in traces) not affecting the overall composition of **2**. We had already established[14,15] that **1** may be placed in concentrated sulfuric acid solutions for months without changes in the ^{13}C NMR spectra and that the nitration in this solvent does not result in sulfonation. Therefore, this almost negligible secondary process may be facilitated by the presence of HCl formed during the chlorination.

All those data showed that the chlorination of **1** is highly regioselective being almost specific below $x = 0.4$ and that the secondary sulfonation is negligible. The chlorination reaction is slow, and its rate decreases rapidly with the degree of conversion that tends to a limit close to the composition [NP($O_2C_{12}H_7Cl$)]$_n$. This strongly suggest that conformational adjustments induced by the incorporation of polar C−Cl bonds to the periphery of the chains render the reactive sites progressively less accessible.

From all the evidence, it can be concluded that the chemical structure of polymer (**2**, $x = 0.3$) is highly regular being very close to that shown in Scheme 1.

The thermal stability of **2** estimated by TGA a 10 °C/min (Experimental Section and Supporting Information) was similar to that of **1** decomposing near 500 °C. However, although the residues left at 800 °C under N_2 were of the order of 50% changing little with x, the residues under air to 900 °C increased with x from 22% ($x = 0.3$) to 40% ($x = 0.75$) [for the starting **1** is 13%]. This fact may account for the slightly low analytical % C mentioned earlier. From the high TGA residues under air (char yield = CR), the limiting oxygen index of those polymers estimated by the Van Krevelen equation (LOI = 17.5 + 0.4CR)[18] was in the range 26−33, which correspond to potential self-extinguishing flame retardants.[18]

The glass transition of the series $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7Cl)_x]\}_n$ (**2**) was detected by DSC but with increasing ambiguity as x increased. However, the data suggested that the T_g are higher than that of the starting polymer **1** (161 °C) changing very little from $x = 0.25$ (173 °C) to $x = 0.75$ (ca. 175 °C). This may be indicating that the high T_g values are more determined by the cyclic nature of the $P(O_2C_{12}H_7Cl)$ groups than by the influence of the peripheral Cl atoms.

In contrast with the free biphenol molecule that can be easily chlorinated[19] and brominated,[20] polymer **1** reacted very slightly (almost negligibly) with bromine in dichloromethane even in the presence of $FeBr_3$ (generated in situ). The reaction was more effective with $AlBr_3$ (also generated in situ adding aluminum metal to the reaction mixture) as clearly revealed by the signals at 820−633 cm^{-1} in the IR spectrum of the products. With iodine no reaction was observed. The iodination however could be achieved using $[Ipy_2]BF_4$ (py = pyridine).[21] Thus, the reaction of **1** with $[Ipy_2]BF_4$ in CH_2Cl_2 in the presence of triflic acid gave the polymers $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7I)]_x\}_n$ (**3**) ($x = 0.4$−1) isolated in ca. 95% yield as pale yellow solids with the expected iodine contents (Scheme 1). To avoid the formation of iodine−phosphazene complexes,[22] sodium thiosulfate was used during the work-up. The isolated products tended to be contaminated with pyridinium triflate (as revealed by the small percent sulfur found by elemental analyses) that was difficult to remove. Being intended for lithiation experiments (see later) they were purified by repeated reprecipitations from THF/water and occasionally THF/aqueous NaOH (see Experimental Section).

Varying the experimental conditions, it was observed that the degree of iodination were always lower than the molar ratio $[Ipy_2]BF_4/(\mathbf{1})$ employed. The reaction was slow requiring at least 30 h, and even with ratios $[Ipy_2]BF_4/(\mathbf{1}) = 2$ it was difficult to reach x values higher than 1. This similarity with the chlorination discussed earlier reinforces the idea that the halogenation induces globular conformations on the polymers hiding the active reaction centers. Also as in the chlorination, exceedingly low amounts of cyclic products from chemical degradation side reactions were detected (extremely weak signals near 25 ppm in the ^{31}P NMR spectra), and the M_w were lower than that of the starting **1** as a result of the chain degradation induced by the acid.[14] The DSC curves showed no well-defined glass transitions, but the estimated T_g values were close to that of **1** changing little with the iodine content, which is consistent with the chlorinated series (see above).

The iodination of the biphenoxy rings was evidenced by the IR spectra that showed two new absorptions at 821 and ca. 620−628 cm^{-1}, not present in the spectrum of **1**. As for the chlorinated derivatives, the first absorption is due to δ-CH modes and the second to C−I stretching modes. Again, the intensity of both bands increased proportionally with x, although the one at 620−628 cm^{-1} was less accurately measured because of the overlapping with the medium-strong band of the parent material at 608 cm^{-1}. The incorporation of iodine atoms was further confirmed by ^{13}C NMR spectroscopy that showed all the expected signals, including the very significant peak at 89 ppm corresponding to the C_5−I carbons.

In sharp contrast with the related chlorine derivatives **2**, the TGA showed that **3** are thermally rather unstable decomposing rapidly above 250 °C by a series of strongly overlapped processes. Furthermore, the residues left in the TGA experiments either under N_2 or air were close to 2%. It seems that the presence of C−I bonds has a very destabilizing effect on **1**.

The potential of polymers **2** and **3** as starting materials to incorporate chemical functions was assessed by applying the well-established silylation method.[23] Well-purified (see above) **2** and **3** were reacted with excess $LiBu^n$ or $LiBu^t$ in THF at −78 °C to generate lithiated reactive intermediates followed by the addition of $ClSiMe_3$. The IR spectra (mainly the bands revealing C−X bonds), elemental analyses (particularly halogen and silicon), and ^1H NMR spectra (intensity ratio Me−Si/aromatics−protons, more accurately measured at 90 °C in DMSO) of the isolated products allowed a good determination of the degree of conversion of halogen into $SiMe_3$.

Repeated experiments with **2** clearly established that the silicon derivatives always contained 40−50% of the initial chlorines unreacted. Their silicon contents however revealed that, considering the fraction of lithiated centers actually created, the silylation step was very efficient. Thus, the product from (**2**, $x = 0.35$) responded within the experimental uncertainties to the composition $\{[NP(O_2C_{12}H_8]_{0.65}[NP(O_2C_{12}H_7Cl]_{0.15}[NP(O_2C_{12}H_7SiMe_3)]_{0.2}\}_n$ (**4**) (see Experimental Section). The ^1H NMR signal of the $SiMe_3$ group was a complex broad multiplet with four very close peaks. This complexity, also reflected in the ^{13}CNMR and ^{29}Si NMR signals, remained in the spectra measured at 90 °C in DMSO. Considering that for $x = 0.2$ most of the $[NP(O_2C_{12}H_7SiMe_3)]$ units would be surrounded by $[NP(O_2C_{12}H_8]$ units, it is likely that the origin of this complexity lies in conformational effects in solution creating various slightly different chemical environments for the $SiMe_3$. However, the influence of the incomplete substitution might also be responsible.

Similar but not identical results were observed from the iodinated **3**. Thus, starting from (**3**, $x = 0.5$) the initial iodine content (21%) dropped to a negligible 0.35%, and the product was $\{[NP(O_2C_{12}H_8]_{0.8}NP(O_2C_{12}H_7Si(CH_3)_3)]_{0.2}\}_n$ (**5**) (Scheme 1) with only 40% of the expected $SiMe_3$ content (the change of x from 0.5 to 0.8 arises from the hydrolytic conversion of the C−Li sites that missed silylation into C−H). Various experiments lead to the same results, occasionally with even less $SiMe_3$ incorporation. This shows that, as might be anticipated, the lithiation is more efficient with the iodobiphenoxy polymers than with the chloro-analogues. The silylation step is however less effective with the higher lithiated chains coming from the iodo-polymers. The degree of conversion of C−Li into C−$SiMe_3$ achieved from **3** was shorter than the observed with analogous polymers having 6,6′-lithiated binaphthoxyphosphazene groups[24] (above 70%) that were more in the usual range of silylation efficiency with lithiated polyphosphazenes using $SiMe_3$ as entering group.[23,25] Considering that these reactions are strongly influenced by the steric effects,[23] those results demonstrate that the proximity of the reactive sites to the main chain reinforces the steric hindrance, limiting its accessibility. In fact, all our attempts to synthesize other derivatives of **1** carrying PPh_2 or PEt_3, groups reacting the lithiated polymers with $PClR_2$ were unsuccessful.

Experimental Section

All reactions were carried out under a dry N_2 atmosphere. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Triflic acid (HSO_3CF_3) and $LiBu^t$ were used as purchased (Aldrich). The 98% sulfuric acid used was very pure (Merck). Chlorine gas was used directly from the bottle purchased (carburos metálicos). CAUTION: all those reagents should always be stored, handled, and used with appropriate care. LiBu^t has been involved in reported accidents. The reagent $[Ipy_2]_2BF_4$ was kindly provided by Professor J. Barluenga (University of Oviedo, see ref 21).

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 already described.[26] The molecular weight distributions (GPC) were similar, having average M_w in the range $(0.5-0.8) \times 10^6$ and polydispersities indexes around 3. Their purity was checked by C, H, N analysis and ^{31}P, ^{1}H NMR and IR spectroscopies. The T_g values were 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, using $CDCl_3$ as solvent unless otherwise stated. ^{1}H and $^{13}C\{^1H\}$ NMR are given in δ relative to TMS ($CDCl_3$ at 77.0 ppm). $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. $^{29}Si\{^1H\}$ NMR are given in δ relative to tetramethylsilane. Coupling constants are in hertz. C, H, N analyses were performed with a Perkin-Elmer 240 microanalyzer. Chlorine, iodine, and silicon 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 wt % solution of tetra-*n*-buthylammonium 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 analysis 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 or 900 °C under constant flow of nitrogen (TGA N_2) or air (TGA air).

Preparation of $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7Cl)]_x\}_n$ (2). The following preparation is representative of all the experiments performed for the chlorination of **1** with 2−10 g scales and various conditions (see text).

Solid **1** (20 g, 87 mmol) was added to 98% H_2SO_4 (150 mL), and the mixture was stirred until a dark brown dense solution was formed. Chlorine gas was then continuously bubbled through the solution with stirring for 5 h. The mixture was poured in small portion in water (2 L) to form a white precipitate that was filtered and washed with plenty of water until pH = 7. The solid was washed with isopropyl alcohol (2 × 200 mL) and diethyl ether (2 × 250 mL), extracting a small fraction of a dark yellow oil. The residue was dried at 50 °C in vacuum. The white solid (20.8 g) was further purified by dissolving it in THF (50 mL) to give of a viscous liquid that was poured in small portions into aqueous 2.5 M NaOH (700 mL). The white precipitate was filtered and washed with plenty of water until pH = 7. The solid was washed with isopropyl alcohol (2 × 100 mL). The final white material $\{[NP(O_2C_{12}H_8)]_{0.7}[NP(O_2C_{12}H_7Cl)_{0.3}\}_n$ (**2**, $x = 0.3$) was dried one night in a vacuum at 50 °C. Yield: 20.2 g, 97%. Anal. Calcd for $C_{12}H_{7.7}NPO_2Cl_{0.3}$ (239.5 g/mol): C, 60.2; H, 3.21; N, 5.84; Cl: 4.45. Found: C, 57.5; H, 3.23; N, 5.88; Cl: 4.75. IR (KBr) cm^{-1}: 3067 m, 3026 w (ν_{CH} arom), 1604 w, 1500 m, 1477 s (ν_{CC} arom), 1387 br s, 1266 sh, 1246 vs, 1194 vs m (ν_{NP}), 1096 s (ν_{P-OCH}), 1040 w, 1013 w, 954 br s, 917 br s, (δ_{POC}), 868 w, 823 w, 786 s, 752 s, 717 m (out-of-plane δ-CH), 648 w (ν-C−Cl), 609 s, 590 m, 538 br s. Relative intensity 648/717 (cm^{-1}) = 0.45. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = -5.8$ ppm. ^{1}H NMR ($CDCl_3$): δ = 7.2 br, 6.90, 6.8 sh ($C_{12}H_8$, $C_{12}H_7$). ^{13}C NMR (ppm, $CDCl_3$): δ = 149 (C2), 129.2, 128.8 (C1, C6, C4), 125(C5), 123(C3) $[(O_2C_{12}H_8)P]$; 147(C2), 131(C1), 128(C5), and 124(C3) $[(O_2C_{12}H_7Cl)P]$ (all much less intense). GPC: M_w 117 000, $M_w/M_n = 2.8$. TGA N_2: −52% (520 °C) (main loss). Residue at 800 °C: 48%. Residue at 950 °C: 26%. TGA air: −36% (510 °C) followed by a continuous loss. Residue at 900 °C: 22%. DSC: T_g = 173 °C (ΔC_p = 0.15 J/(g K)).

The polymer $\{[NP(O_2C_{12}H_8]_{0.25}NP(O_2C_{12}H_7Cl)]_{0.75}\}_n$ (**2**, $x = 0.75$) was similarly obtained in 96% yield from $[NP(O_2C_{12}H_8]$ (10 g, 44 mmol) in 98% H_2SO_4 (150 mL) and chlorine (10 h). Anal. Calcd for $NPO_2C_{12}H_{7.25}Cl_{0.75}$ (254.9 g/mol): C, 56.5; H, 2.84; N, 5.49; Cl: 10.37. Found: C, 53.9; H, 2.84; N, 5.78; Cl: 10.14. IR (KBr) cm^{-1}: 648/717 (cm^{-1}) = 0.75. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = -5.3$ ppm. ^{1}H NMR ($CDCl_3$): δ = 6.9 m, br ($C_{12}H_8$, $C_{12}H_7$). GPC: M_w 155 000, $M_w/M_n = 2.7$. TGA N_2: −51% (520 °C) (main loss). Residue at 800 °C: 49%. TGA air: −40% (510 °C) and a continuous loss. Residue at 900 °C: 40%. DSC: T_g = 175 °C (ΔC_p = 0.6 J/(g K)).

Preparation of $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7I)]_x\}_n$ (3). The following preparation is representative of all the experiments performed for the iodination of **1** with 0.5−1 g scales and various conditions (see text).

To a solution of **1** (0.5 g, 2.18 mmol) in CH_2Cl_2 (50 mL), $[Ipy_2]BF_4$ (0.8 g., 2.15 mmol) was added, and after stirring for 15 min at room temperature, the triflic acid (HSO_3CF_3) (0.42 mL, 4.4 mmol, in 15 mL of CH_2Cl_2) was added dropwise. The mixture (that turned red from the beginning) was stirred for 30 h at room temperature, half of the solvent was evaporated in a vacuum, and the concentrated solution was poured into 1 L of aqueous $Na_2S_2O_3$ (15 g/L). The resulting suspension was stirred for 1 h (until no more discoloration was observed) and filtered. The solid was washed with water, stirred again with 250 mL of water for 1 h, filtered, and dried in a vacuum at 40 °C to give (**3**, $x = 0.5$) as a yellow solid. Yield: 0.62 g (97.3%). The product had to be repurified from some pyridinium triflate by reprecipitating from THF/water and THF/aqueous NaOH. Anal. Calcd for $C_{12}H_{7.5}NPO_2I_{0.5}$ (292): C 49.3, H 2.57, N 4.79, I 21.7. Found: C 48.6, H 2.65, N 6.63, I 20.0 (%S negligible). M_w (GPC): 163 000 (PDI = 1.94). IR (KBr) cm^{-1}: 3065 m, 3026 w (ν_{CH} arom), 1606 vw, 1500 m, 1476 s (ν_{CC} arom), 1420 sh, 1379 br s (typical of dioxybiphenylphosphazenes, not assigned), 1266 sh, 1246 vs, 1194 vs m (ν_{NP}), 1096 s (ν_{P-OCH}), 1041 w, 1014 w, 953 br s, 918 s (δ_{POC}), 821 m, 786 s, 752 s, 716 m (out-of-plane δ-CH), 628 w, 608 s, 538 br s. ^{31}P NMR (ppm, $CDCl_3$): −5.5. ^{1}H NMR (ppm, $CDCl_3$): 7.2 br, 6.90 br (CH aromatic rings). ^{13}C NMR (ppm, $CDCl_3$): δ = 149 (C2), 129.4, 128.8 (C1, C6, C4), 125 (C5), 123 (C3) $[(O_2C_{12}H_8)P]$; 138 (C2), 132, 129.6 (C1, C6, C4), 127 (C3), 89(C5) $[(O_2C_{12}H_7I)P]$. TGA: A continuous loss from 200 to 800 °C. Residue at 800 °C: 7%. Further loss of 5% after prolonging the heating at 800 °C for 1 h, leaving an stabilized residue. TGA air: continuous loss. Residue at 900 °C 2%. T_g = 160 °C, C_p = 0.30 J/(g K).

Silylations Experiments with $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7Cl)]_x\}_n$ (2). The experiment described below is representative of many others that were conducted that lead to very similar results. Increasing the LiR molar ratio or changing to LiBu^n did not alter the main conclusions.

Polymer (**2**, $x = 0.35$) (0.5 g, 2.1 mmol, 0.63 mmol of Cl) was dissolved in THF (50 mL). The solution was cooled to −78 °C, and LiBu^t (1.8 mL, 1.7 M, 3.05 mmol) (see caution note above) was added slowly; the mixture was stirred at this temperature for 2 h. Then, $ClSi(CH_3)_3$ (1.5 mL, 12.2 mmol) was added, and the reaction mixture was stirred at −78 °C to room temperature for one night. The solution was concentrated in a vacuum to viscous liquid and poured portion-wise (Pasteur pipet) into water (100 mL) to form a white precipitate, which was washed with CH_3OH. The purification was performed by reprecipitation from THF (5 mL)/CH_3OH (50 mL) and washing with diethyl ether. The final white material (**4**) was dried one night in a vacuum at 50 °C. Yield: 0.47 g, 90.4%. Anal. Calcd for $\{[NP(O_2C_{12}H_8]_{0.65}[NP(O_2C_{12}H_7Cl)]_{0.15}[NP(O_2C_{12}H_7Si(CH_3)_3)]_{0.2}\}_n$: $NPO_2C_{12.6}H_{9.45}Cl_{0.15}Si_{0.2}$ (248.7 g/mol): C, 60.8; H, 3.80; N, 5.63; Cl, 2.14 ; Si, 2.25. Found: C, 59.8; H, 4.09; N, 5.71; Cl, 2.5 Si, 2.0. IR (KBr) cm^{-1}: ν = 3066 w, 3028 w (ν-CH-arom), 2952 w, 2893 w (ν-CH−Si(Me)$_3$), 1501 w, 1477 m (ν-C=C-arom), 1374 m, br (not assigned), 1247 vs 1195 vs, (ν-PN), 1096 s (ν-P−OCH), 953 vs, br, 920 s, br (δ-POC), 856 m, br, 840 m, 786 s, 751 s, 717 m, 655 w (ν-C−Cl), 609 m, 591 w, 537 m, br. $^{31}P\{H\}$ NMR (CD_2Cl_2): $\delta = -5.7$ ppm. ^1H NMR (CD_2Cl_2): $\delta = 7.3$, 7.0, 6.8 m, br ($C_{12}H_8$, $C_{12}H_7$), −0.3, −0.18, −0.00, −0.12 m, br (CH_3). Intensity ratio Me−Si/aromatics = 0.27 (expected for the proposed formula = 0.24). $^{13}C\{H\}$ NMR (CD_2Cl_2): $\delta =$ 149, 129.3, 129,1, 128,9, 125. 122.6 ($C_{12}H_8$, $C_{12}H_7$), −1.0, −1.1, −1.4, −1.6, −1.7 m (Me_3Si).$^{29}Si\ \{H\}$ NMR (CD_2Cl_2): $\delta = -2$, −2.4, −3.5 br m. GPC: M_w 122 000, M_w/M_n = 3.4.

Silylations Experiments with $\{[NP(O_2C_{12}H_8)]_{1-x}[NP(O_2C_{12}H_7I)_x\}_n$ (3). The experiment described below is representative of many others that were conducted that lead to very similar results. Increasing the LiR molar ratio or changing to LiBu did not alter the main conclusions.

Polymer (**3**, $x = 0.5$) (0.15 g, 0.51 mmol, 0.26 mmol of I) was dissolved in THF (50 mL). The solution was cooled to −78 °C, $LiBu^t$ (0.4 mL 1.7 M, 0.7 mmol) (see caution note above) was added slowly, and the mixture was stirred at this temperature for 2 h. Then, $ClSi(CH_3)_3$ (0.36 mL, 0.28 mmol) was added, and the reaction mixture was stirred from −78 °C to room temperature and then overnight. The solution was concentrated in a vacuum to a viscous liquid that was poured into water (100 mL) to form a white precipitate, which was washed with CH_3OH. The purification was performed by dissolving the product in THF (5 mL) and pouring portion-wise (Pasteur pipet) into CH_3OH (50 mL) to give a precipitate that was washed with diethyl ether. The final white powder (**5**) was dried one night in a vacuum at 50 °C. Yield: 0.1 g, 74%. Anal. Calcd for $\{[NP(O_2C_{12}H_8]_{0.8}NP\ (O_2C_{12}H_7Si(CH_3)_3)]_{0.2}\}_n$. $NPO_2C_{12.6}H_{9.6}Si_{0.2}$ (243.4 g/mol): C, 62.1; H, 3.94; N, 5.75; Si, 2.30. Found: C, 59.6; H, 3.85; N, 5.81; Si, 3.0. Residual I: 0.35%. IR (KBr) cm^{-1}: ν = 3066 w, 3031 w (ν-CH-arom), 2953 w, 2892 w (ν-CH−Si(Me)$_3$), 1501 w, 1478 m (ν-C=C-arom), 1367 m, br (not assigned), 1246 vs 1197 vs, (ν-PN), 1096 s (ν-P−OCH), 952 vs, br, 920 s, br (δ-POC), 860 m, br, 838 m, 786 s, 751 s, 717 m, 655 w (ν-C−Cl), 609 m, 591 w, 538 m, br. $^{31}P\{H\}$ NMR ($CDCl_3$): $\delta = -6.4$ ppm. ^1H NMR ($CDCl_3$): $\delta =$ 7.2, 6.8, 6.7 m, br ($C_{12}H_8$, $C_{12}H_7$), 0.0 br (CH_3). Intensity ratio Me−Si/aromatics = 0.20 (expected for the proposed formula = 0.23). GPC: M_w 167 000, M_w/M_n = 2.3.

Conclusions

The direct reaction of the phosphazene $\{[NP(O_2C_{12}H_8)]\}_n$ with Cl_2 has led to a new type of well-defined chemically regular chlorinated polyphosphazenes that may be potential self-extinguishing flame retardants. The reaction with $[Ipy_2]BF_4$ gave the iodine derivatives that are thermally unstable leaving 2% TGA residues.

The use of the silylation method revealed that while the lithiation of the chlorine derivatives reached ca. 50%, the iodine analogues could be almost completely lithiated. The conversion of the generated C−Li sites into C−$SiMe_3$, however, was below the efficiency usually observed with polyphosphazenes.

Clearly, the chemical reactivity of polyphosphazenes with 2,2′-dioxybiphenylphosphorus rings in the repeating units is limited by conformational changes induced by the new groups incorporated to the ring carbons and by the proximity of the reaction centers to the main chain.

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Supporting Information Available: IR spectrum (KBr pellet) of polymer $\{[NP(O_2C_{12}H_8]_{0.25}[NP(O_2C_{12}H_7Cl)]_{0.75}\}_n$; ^{13}C NMR spectra (CD_2Cl_2) of polymer $\{[NP(O_2C_{12}H_8)]_{0.5}[NP(O_2C_{12}H_7Cl)]_{0.5}\}_n$ (Jmod and Dept 3); and TGA curves (and their derivatives) for polymers $\{[NP(O_2C_{12}H_8)]_{1\text{-}x}[NP(O_2C_{12}H_7Cl)]_x\}_n$ from 50 to 900 at 10 °C/min under air. This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) (a) Allcock, H. R. *Chemistry and Applications of Polyphosphazenes*; Wiley: New York, 2003. (b) Marck, J. E.; Allcock, H. R.; West, R. *Inorganic Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1992.
(2) De Jaeger, R.; Gleria, M. *Phosphazenes: A Worldwide Insight*; NOVA Sci. Publ: New York, 2005.
(3) (a) Allcock, H. R. *Appl. Organomet. Chem.* **1998**, *12*, 659–666. (b) Ibid., Chapter 8, p 262.
(4) Allcock, H. R.; Fitzpatrick, R. J. *Chem. Mater.* **1991**, *3*, 1120–1132.
(5) Allcock, H. R. *Chem. Mater.* **1994**, *6*, 1476–1491.
(6) Gleria, M.; Minto, F.; Po, R.; Cardi, N. L.; Fiocca, L.; Spera, S. *Macromol. Chem. Phys.* **1998**, *199*, 2477–2487.
(7) Andrianov, A. K.; Marin, A.; Chen, J.; Sargent, J.; Corbett, N. *Macromolecules* **2004**, *37*, 4075–4080.
(8) Carriedo, G. A.; García-Alonso, F. J.; González, P. A.; Gómez-Elipe, P. *Polyhedron* **1999**, *18*, 2853–2859.
(9) See ref 1a, Chapter 8, p 262 and ref 2, Vol 1. Part 1, Chapter 5, p 212.
(10) Carriedo, G. A. Synthesis and chemical regularity in phosphazene copolymers. In *Polyphosphazenes for Biomedical Applications*; Andrianov, A. K., Ed.; John Wiley & Sons: Hoboken, NJ, 2009; Chapter 19, p 379.
(11) See ref 1a and Olshavsky, M. A.; Allcock, H. R. *Macromolecules* **1995**, *28*, 6188–6197.
(12) (a) Carriedo, G. A.; Fernández Catuxo, L.; García Alonso, F. J.; Gómez Elipe, P.; González, P. A. *Macromolecules* **1996**, *29*, 5320–5325. (b) Carriedo, G. A.; García Alonso, F. J.; Gómez Elipe, P.; González, P. A.; Marco, C.; Gómez, M. P.; Ellis, G. J. *Appl. Polym. Sci.* **2000**, *77*, 568–576.
(13) Laguna, M. T.; Tarazona, M. P.; Carriedo, G. A.; García Alonso, F. J.; Fidalgo, J. I.; Saiz, E. *Macromolecules* **2002**, *35*, 7505–7515.
(14) Carriedo, G. A.; García Alonso, F. J.; García Alvarez, J. L.; Presa Soto, A.; Tarazona, M. P.; Laguna, M. T. R.; Marcelo, G.; Mendicuti, F.; Sáiz, E. *Macromolecules* **2008**, *41*, 8483–8490.
(15) Carriedo, G. A.; Presa-Soto, A.; Valenzuela, M. L. *Macromolecules* **2008**, *41*, 6972–6976.
(16) (a) Bellami, L. J. *The Infrared Spectra of Complex Molecules*, 3rd ed.; Chapman and Hall: London, 1975; Vol *1*, p 84. (b) Ibid., p 368.
(17) Alexakis, A.; Polet, D.; Rosset, S.; March, S. *J. Org. Chem.* **2004**, *69*, 5660–5667.
(18) Zhang, T.; Jin, R.-g. *Adv. Mater. Res.* **2006**, *11−12*, 395–398.
(19) DeJongh, D. C.; Van Fossen, R. Y. *J. Org. Chem.* **1972**, *37*, 1129–1135.
(20) Gómez-Lor, B.; Echavarren, A. M.; Santos, A. *Tetrahedron Lett.* **1977**, *33*, 5347–5350.
(21) Barluenga, J.; González, J. M.; García-Martín, M. A.; Campos, P. J.; Asensio, G. *J. Org. Chem.* **1993**, *58*, 2058–2060.
(22) Lerner, M. M.; Tipton, A. L.; Shriver, D.; Dembeck, A. A.; Allcock, H. R. *Chem. Mater.* **1991**, *3*, 1117–1120.
(23) Allcock, H. R.; Nelson, C. J.; Coggio, W. D.; Manners, I.; Koros, W. J.; Walker, D. R. B.; Pessan, L. A. *Macromolecules* **1993**, *26*, 1493–1502.
(24) Carriedo, G. A.; García Alonso, F. J.; Presa Soto, A. *Macromolecules* **2006**, *39*, 4704–4709.
(25) Carriedo, G. A.; Valenzuela, M. L.; Díaz, C.; Ushak, S. *Eur. Polym. J.* **2008**, *44*, 686–693.
(26) Carriedo, G. A.; García alonso, F. J.; Gómez-Elipe, P.; Fidalgo, J. I.; García-Alvarez, J. L.; Presa-Soto, A. *Chem. Eur. J.* **2003**, *9*, 3833–3836.