Chiral 6,6′-Disilylated Binaphthoxyphosphazene Copolymers Carrying Diphenyl−Phosphine−Phenoxy Groups Inside Wide Chiral Pockets†

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ABSTRACT: The reaction of the chiral phosphazene copolymer $\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**I**) [$(O_2C_{20}H_{10}Br_2)$ = R-6,6′-dibromo-2,2-dioxy-1,1′-binaphthyl] with ^{t}BuLi in THF gave the intermediate $\{[NP(O_2C_{20}H_{10}Li_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**II**) that was treated with the chlorosilanes $SiR_1R_2R_3Cl$ to give the new polyphosphazenes $\{[NP(O_2C_{20}H_{10}\{SiR_1R_2R_3\}_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ [$R_1R_2R_3 = Me_3$ (**III**), $R_1R_2R_3 = Me_2$-Ph (**IV**), $R_1R_2R_3 = MePh_2$ (**V**), $R_1R_2R_3 = Ph_3$ (**VI**)], in which the phosphine ligands are located inside sterically demanding chiral pockets. The almost inevitable presence of oxidized $OC_6H_4P(O)Ph_2$ groups in those polymers was successfully resolved by a quantitative removal of the oxygen by the $SiHCl_3/PPh_3$ method that was adapted to high M_w polymers. The new polyphosphazenes had M_w of the order of 10^6, exhibited high thermal stabilities and were liquid crystalline at room temperature.

Introduction

The polyphosphazenes are very interesting compounds in basic and applied material science.[1] Following the discovery of the polyphosphazene with the cyclic repeating units $[NP(O_2C_{12}H_8)]_n$ [$(O_2C_{12}H_8)$ = 2,2′-dioxy-1,1′-biphenyl],[2] we reported the synthesis of the related but optically active poly(binaphthoxyphosphazene) $[NP(O_2C_{20}H_{12})]_n$ [$(O_2C_{20}H_{12})$ = 2,2′-dioxy-1,1′-binaphthyl].[3] Several studies have shown that this polymer have an helical secondary structure with one screw sense preference.[4] In solution, it behaves as a random coil[5] exhibiting luminescence properties that are dependent on the helicity,[6] and in the amorphous solid state it forms a columnar hexagonal packing.[7]

Various types of random copolymers combining binaphthoxyphosphazene units with other functionalized aryloxyphosphezene units were obtained to show that the chemical functions in the former are in chiral environments[8] (chiral pockets), and some were used as supported catalysts for the hydrogen transfer from isopropyl alcohol to acetophenone.[9] The results indicated that, though the catalysts were active, no enantiomeric excesses (ee) were observed. Thus, considering that the presence of bulky substituents in the 6,6′-positions of the binaphthyls would help to increase the steric effects necessary to promote enantioselectivity in asymmetric reactions, we undertook the synthesis of new copolymers carrying phosphine ligands inside larger chiral pockets amplified by introducing silane groups in the 6,6′-binaphthyl positions (see Figure 1).

The incorporation of functional groups in polyphosphazenes is a very important subject on itself because it gives new opportunities to the design of materials with predetermined properties,[10,11] particularly in the case of the polymers carrying chiral binaphthoxy substituents. Another point of relevance is to test synthetic routes to derivatize polyphosphazenes by reactions carried out directly on the polymers,[10] a field that presents various points of great interest such as, among others, the introduction of sulfonic acid functionalities,[12] carboxylic acid functionalities,[13] and amino aryloxy groups[14] or attaching other polymer chains to polyphosphazenes.[15]

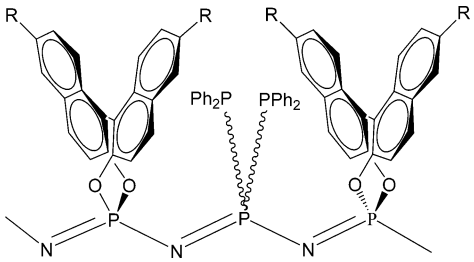

Figure 1.

It is known that incorporation of bromoaryloxy derivatives to polyphosphazene leads to useful synthetic polymer precursors by lithiation,[16] and recently, we have reported the synthesis of the enantiomerically pure 6,6′-dibromo-substituted poly(binaphthoxyphosphazene).[17] We have also reported that it is possible to obtain chiral phosphazene copolymers carrying phosphine ligands,[8] but they invariably contained a fraction of the PPh_2 groups oxidized to $P(O)Ph_2$.

Herein we describe the successful lithiation of copolymers of the type $\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ [$(O_2C_{20}H_{10}Br_2)$ = 6,6′-dibromo-2,2′-dioxy-1,1′-binaphthyl) and their reaction with chlorosilanes to give new optically active poly(binaphthoxyphoshazenes) having phosphine ligands inside very amplified chiral pockets, that were completely free of oxidized sites by using the method[18] based on the utilization of a mixture of $SiHCl_3/PPh_3$, but specially adapted to high molecular weight polymers. The spectroscopic properties and the X-ray diffraction of the new polymers have also provided with several observations that are very useful in the characterization of polymeric materials.

Results and Discussion

Following the method reported earlier,[8] the copolymer $\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**I**), that carries useful phosphine ligands was synthesized reacting $[NPCl_2]_n$ first with R(+)-2,2′-dihydroxy-6,6′-dibromo-1,1′-binaphthyl and subsequently with $HOC_6H_4PPh_2$, in refluxing THF in the presence

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† Dedicated to Professor Víctor Riera González.

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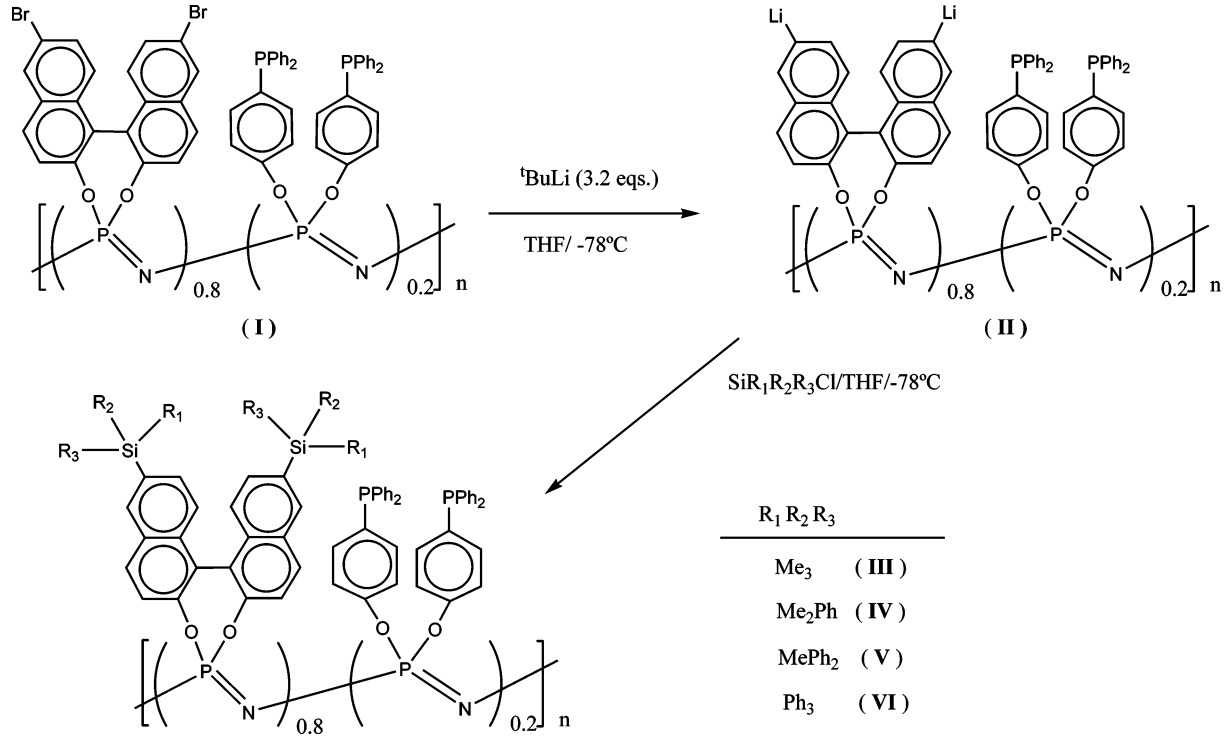
Scheme 1



of Cs_2CO_3. The material was obtained as a yellow solid with M_w of the order of 1.7×10^6, and a small fraction (12%) of the phosphines oxidized to $O-C_6H_4-P(O)PPh_2$ (that was observed to increase with time in the stored solid samples).

The reaction of (**I**) with ^{t}BuLi in THF at low temperature yielded the 6,6′-dilithiated derivative (**II**) (see Scheme 1, where for simplicity, the fraction of oxidized phosphine sites are not shown, which, as it will be seen later, was unimportant). Various experiments demonstrated that the optimized conditions were 3.2 equiv of ^{t}BuLi in THF at −78 °C during 1.5 h to give a turbid greenish solution. It was checked that the addition of water to this reagent resulted in the quantitative formation of the polymer of formula $\{[NP(O_2C_{20}H_{12})]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ having less than 0.5% bromine, that was very similar to the material obtained from $[NPCl_2]_n$ first with *R*-(+)-2,2′-dihydroxy-1,1′-binaphthyl and subsequently with $HOC_6H_4PPh_2$ but having 90% of the binaphthoxyphosphazene units.[8]

The addition of the chlorosilanes $SiR_1R_2R_3Cl$ [$R_1R_2R_3 = Me_3$; Me_2Ph; $MePh_2$ or Ph_3] gave the derivatives $\{[NP(O_2C_{20}H_{10}\text{-}\{SiR_1R_2R_3\}_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**III**−**VI**) (see Scheme 1) that were isolated as yellow solids in 70−80% yield.

It should be noted that the preparation of those polymers from the silyl-substituted binaphthols would have required the synthesis of the latter involving various protection and deprotection steps, while the binaphthyls attached as binaphthoxyphosphazene units can be considered as already protected and not requiring the reconversion into the binaphthols. Also, is very likely that the necessary substitution reactions of the binaphthols with the starting $(NPCl_2)_n$ would present many difficulties.

The M_w (GPC) of the new polymers were between 10^6 and 2×10^6 with polydispersity indexes (PDI) around 2−3 (Table 1). All were optically active as shown by their specific rotations (that, because of the yellow color, and like the parent dibromo derivative[8] had to be measured with the 578 nm Hg line). The data (Table 1) showed that the specific rotation shifted to more negative values as more phenyl rings were incorporated to the silyl groups.

Table 1. M_w, Specific Rotation, and X-ray Data for the New Polymers[a]

polym	$M_w \times 10^{-6}$ (IPD)[b]	$[\alpha]_{578}$[b]	$M_w \times 10^{-6}$ (IPD)[c]	$[\alpha]_{578}$[c]	2θ (deg)	d (Å)[e]
I	1.8 (1.9)	+10	1.1 (2.1)	+14	5.5	16.0
III	1.1 (2.6)	+13	0.5 (3.3)	+16	4.26	20.7
IV	1.5 (2.8)	−2	0.9 (3.1)	−4	4.39	20.1
V	2.2 (3.0)	−63	*d*	*d*	4.35	20.3
VI	1.0 (2.6)	−83	*d*	*d*	4.43	19.9

[a] $[\alpha]_{578}$ in $CHCl_3$ at 0.5c. near 20 °C. [b] Oxidized materials. [c] Polymers free of $P(O)Ph_2$. [d] Insoluble. [e] For the nonsubstituted derivative with two H atoms in the 6,6′-positions the values are 7.5 (11.8).

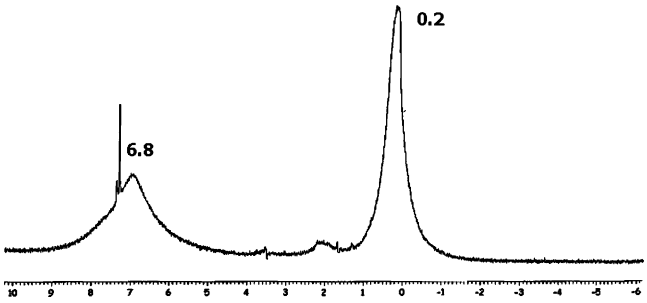
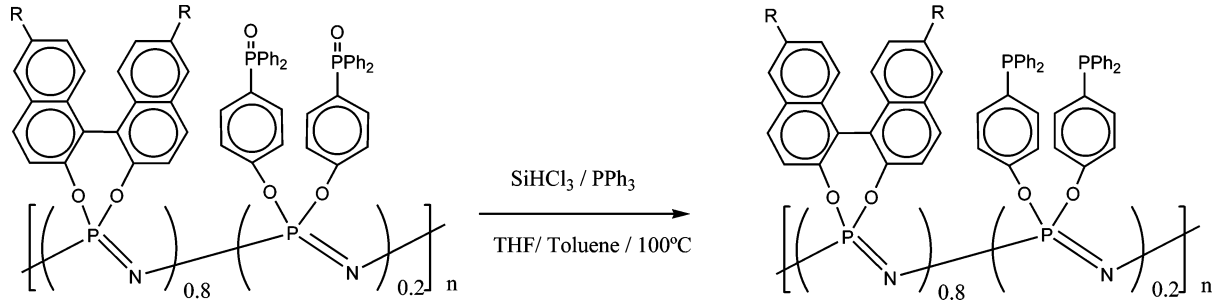


Figure 2. ^{1}H NMR spectrum of **III** in $CHCl_3$.

All the spectroscopic data were in accord with the expected formulation. Very informative were the IR spectra that, apart from the very strong ν_{PN} absorptions at ca. 1250 and 1215, showed the bands at 2954 and 2896 attributable to the ν_{CH} aliphatic protons, another at 1428 corresponding to the aromatic protons of the silane moieties and one or two bands between 830 and 750 attributable to methyl rocking.[19] The attachment of the $SiR_1R_2R_3$ groups to the binaphthyl ring was also confirmed by the strong band at ca. 1110 corresponding to aromatic ring deformation.[19] But particularly useful were the ^{1}H NMR spectra (see Figure 2 and Experimental Section), which showed the broad signal of the Me protons of the silane (centered at ca. 0 ppm) with the expected integrals relative to the signal of the aryl protons (broad signal centered near 7 ppm),

Scheme 2



indicating that more that 95% of the original Br atoms were substituted by the SiR_3 groups).

The ^{31}P NMR spectra showed the two expected broad signals for the phosphorus of the polymeric chain (the $[NP(O_2C_{20}H_{12})]$ at −3 ppm, and the $[NP(OC_6H_4-PPh_2)_2]$ at −20 ppm), and the sharp singlet at −6.8 for the PPh_2 groups. However, the spectra also showed the singlet at 28 ppm indicating the presence of oxidized phosphine centers [$OC_6H_4P(O)Ph_2$ groups], always in a much higher proportion (close to the totality) that in the starting material. The oxidation of the phosphines has been repeatedly observed by us in many syntheses of phosphine containing polyphosphazenes even taking the usual precautions.[8,20,21] This is clearly due to the facile oxidation of the $-OC_6H_4PPh_2$ groups that are present in very small amounts in relation to the large quantities of solvents used during the workup for the isolation of the polymers. Thus, even using deoxygenated solvents a fraction of the phosphines is always affected. In fact, this is similar to what may happen during the synthesis of the phosphines $HO-C_6H_4-PPh_2$, but, while the latter can be purified, at the polymer level it is not possible to separate the $-OC_6H_4PPh_2$ from the $-OC_6H_4P(O)Ph_2$ that are present in the same chain.

To eliminate that P(O) groups from all the polymers, we considered the method based on the reaction with $SiHCl_3$ in the presence of PPh_3 as the sacrificial phosphine[18] but adapting the workup to the special characteristics of our polymeric materials (see Experimental Section). To optimize the conditions of the method we reacted the dibromo derivative (**I**) (having almost 50% of the PPh_2 oxidized) with PPh_3 and $SiHCl_3$ overnight in a mixture of THF/toluene (1:1) at 100 °C (see Scheme 2), followed by addition of cold (0 °C) deoxygenated methanol (that transformed the excess of silane in the soluble $Si(OMe)_4$ while causing the precipitation of the polymer but, at the same time, maintaining the PPh_3 in solution) and finally solid K_2CO_3 (to remove the acids). The yellow precipitate obtained was washed with water (that easily dissolved the potassium salts) and methanol and dried in vacuo to give the oxygen-free polymer $\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**I**) in 90% yield. The complete removal of the oxygen was noted not only in the ^{31}P NMR spectrum (see Figure 3) but, interestingly, also in the 600−500 cm^{-1} region of the IR spectrum. Thus, the initial oxidized material exhibited two strong bands (see Figure 4), one at 575 and other at 538 cm^{-1} while only the former could be observed in the spectrum of the oxygen-free material. The latter band is clearly attributable to the $P(O)R_2$ groups.[22]

All these observations are useful in the synthesis and characterization of polymers carrying supported phosphines, especially when they are insoluble and no NMR data can be easily acquired.

Following the same procedure carried out with (**I**), the polymers $\{[NP(O_2C_{20}H_{10}\{SiR_1R_2R_3\}_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**III**−**VI**) were obtained completely free of oxidized phosphines in 90% yield. The analytical data (Experimental Section) were in accord with the formula proposed (within the errors that can

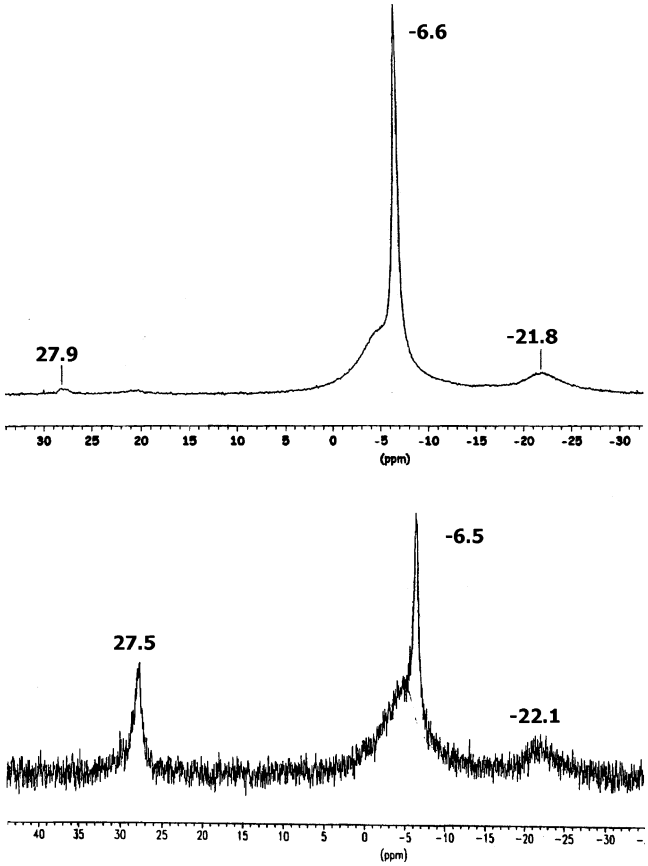


Figure 3. ^{31}P NMR spectra of **I**: (a) oxidized; (b) free of oxygen.

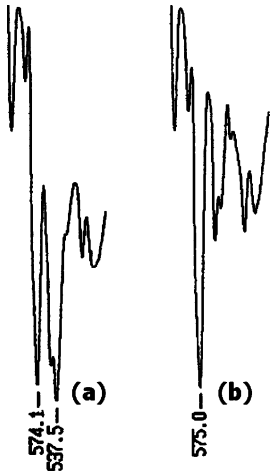


Figure 4. IR spectra of **I**: (a) oxidized; (b) free of oxygen.

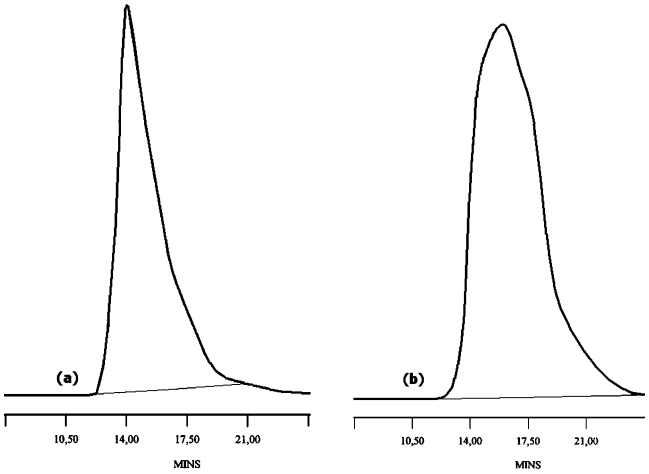


Figure 5. GPC chromatograms of polymer **III**: (a) containing $C_6H_4P(O)Ph_2$ groups; (b) after deoxygenation.

be acceptable with that kind of random copolymers). The deviations were more significant for the polymers with higher C_6H_5 contents, especially for polymer **VI**. This could be attributed to the formation of silicon carbides during the combustion, but it is also possible that, in this case, the composition of the material isolated may deviate from the idealized one, because its is known that the incorporation of silyl groups with C_6H_5 fragments has also encountered experimental difficulties in other lithiated aryloxyphosphazenes.[23] However, the presence of the $SiMe(C_6H_5)_2$ or $Si(C_6H_5)_3$ in polymers **V** and **VI** could be unambiguously established by the IR spectra that (apart from the total absence of the bands at 538 cm^{-1} of the P(O)Ph), showed an intense sharp absorption at 1428 cm^{-1} (attributable to one of the ν_{CC} aryl modes) that was not observed in the IR of the $SiMe_3$ derivative (**III**) and with much less intensity in the IR of the $SiMe_2Ph$ derivative (**IV**). Also consistent were the relative intensities of the aliphatic ν_{CH} band at 2954 cm^{-1} (absent in the case of **VI**) and the aromatic ν_{CH} band at 3065 cm^{-1} (much more intense in the IR of **V** and **VI**).

The decreasing solubility with the number of phenyl groups in the silyl moieties made the polymers **IV** and **V** only sparingly soluble, and therefore, their M_w (GPC) and their specific rotation in solution could not be accurately measured.

The molecular weight distributions of the polymers obtained were apparently different from those of the starting oxidized materials that had almost double average M_w's (see Table 1 and Figure 5). This, however, should be considered with caution because it is known that in the case of phosphazenes,[24] and especially if they contain phosphines,[20] the measurement of M_w by GPC can be easily distorted by the behavior of those macromolecules in solution even in the presence of ammonium salts. Therefore, the M_w of the oxidized and oxygen free polymers (including the insoluble ones) should be considered in the same range of magnitude. Similar considerations apply to the values and tendencies of the specific rotations (see Table 1).

The TGA thermograms (that were very similar to those obtained for the oxidized samples) evidenced that the new polymers are thermally stable. Up to 250 °C they only lost ca. 5%, corresponding to retained solvents. Fast decomposition began near 300 °C above (the weight loss of about 50−60% is centered at about 450 °C) and the residues left after 800 °C (not yet stabilized) were in the range 25−50%.

The DSC curves showed no abrupt heat capacity changes attributable to a glass transition and therefore the T_g could not be measured. The values, however, must be of the order than those of the related dibromobinaphthoxyphosphazene[8] (T_g = 256 °C) and the completely unsubstituted derivative[8] (T_g = 268 °C).

The X-ray diffractograms of the new polymers showed that they are amorphous, but the presence of a well-defined broad reflection at very low angles (Figure 6 and Table 1) indicated that, according to the usual explanation[25] they are liquid crystalline materials with a smectic structure. Moreover, comparing the data (Table 1) it could be observed that the SiR_3 substituents in the 6,6′-positions generate larger interplanar distances (ca. 20 Å) than the unsubstituted, $\{[NP(O_2C_{20}H_{12})]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$, (11,8 Å) and the bromo derivative, $\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$, (16 Å). We have detected similar tendencies in other phosphazene copolymers with biphenoxy or binaphthoxy units, but as a function of the substituents in the $[NP(OR)_2]$ units.[26] However, considering that as we have also shown,[7] the packing of the helical binaphthoxyphosphazene chains follows a hexagonal pattern, it is also possible that the wide angle reflection could be attributed to the interchain columnar separation rather than to the interplanar distance.

Experimental Section

All reactions were carried out under a dry N_2 atmosphere. K_2CO_3 was dried at 140 °C prior to use. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Methanol was distilled from a mixture of Mg and iodine.

^{t}BuLi (1.7 M in pentane) and the silanes $SiMe_3Cl$, $SiMe_2PhCl$, $SiMePh_2Cl$ and $SiPh_3Cl$, $SiHCl_3$ were used as purchased (Aldrich).

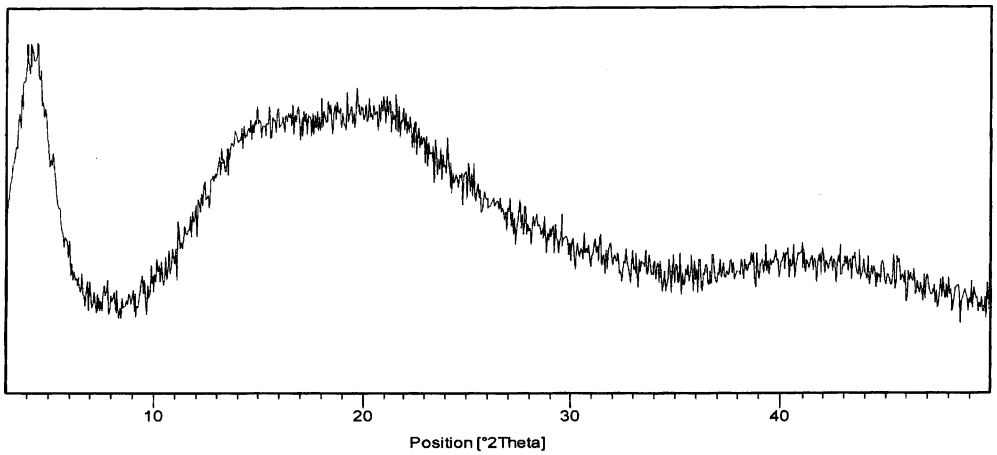


Figure 6. X-ray diffractogram of polymer **III**.

Table 2

R_1, R_2, R_3	g of **I** (mmol)	mL of ^{t}BuLi (mmol)	$ClSiR_1R_2R_3$, g or mL (mmol)	yield, %
Me, Me, Ph (**IV**)	0.3 (0.59)	1.1 (1.88)	0.38 mL (2.25)	78
Me, Ph, Ph (**V**)	0.3 (0.59)	1.1 (1.88)	0.47 mL (2.25)	68
Ph, Ph, Ph (**VI**)	0.3 (0.59)	1.1 (1.88)	0.78 g (2.63)	70[a]

[a] The insoluble polymer was only washed with water, methanol, and ether.

The polymer $\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}][NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (**I**) was prepared as published earlier.[8]

The IR spectra were recorded with a Perkin-Elmer FT Paragon 1000 spectrometer. NMR spectra were recorded on Bruker AC-200, DPX-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. Coupling constants are in Hz. C, H, N, analyses were performed with a Perkin-Elmer 240 microanalyzer. Cl, Br, and Si 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*-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. DSC experiments were carried out with a Mettler DSC 300 differential scanning calorimeter equipped with a TA 1100 computer at scan rate of 10 °C min^{-1}. 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 and maintained at 800 °C for an additional $^1/_2$ h.

The specific optical rotations [α] were measured with a Perkin-Elmer 241 polarimeter at the Hg line of 578 nm near 25 °C in $CHCl_3$.

X-ray diffractograms were measured with PANalytical X'Pert Pro, using Kα_1 Cu radiation (1.5406 Å) at 45 kV-40 mA, with a X'Celerator detector with 2.122°. The scans were $\theta/2\theta$ from 2 to 50° in 2θ at 0.033° intervals at 300 s per interval.

$\{[NP(O_2C_{20}H_{10}Br_2)]_{0.8}][NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ (I) (Oxygen Free). The polymer was obtained as indicated in ref 8 and freed of $P(O)Ph_2$ groups by the procedure indicated later for polymer **III**−**VI**.

Anal. Calcd. for $C_{23.2}H_{13.6}O_2NP_{1.4}Br_{1.6}$ (509.57): C, 54.7; H, 2.69; N, 2.75; Br, 25. Found: C, 53.1; H, 2.9; N, 2.9; Br, 26.

IR (cm^{-1}, KBr pellets): 3053 w (ν_{CH} arom), 1585 m, 1493 m, 1434 w, 1396 w, 1354 w (ν_{CC} arom), 1317 m (ν_{C-OP}), 1256 m, 1218 s, 1191 m, 1167 m (ν_{NP}), 1066 m (ν_{P-OC}), 960 s, 943 s(δ_{POC}), 874 m, 826 m, 807 m (δ_{PNP}), 778 w, 742 w, 728 w, 693 w, 656 w, 601 w, 570 m (δ_{NPO}), 533 w, 493 w, 472 w.

^1H NMR ($CDCl_3$, 25 °C): δ = 5.5−9.5 (very br m, aromatic rings).$^1P\{^1H\}$ NMR ($CDCl_3$, 25 °C): 27.9 (m, ($OC_5H_4P(O)Ph_2$) (negligible amount, see Figure 3), -4.2 (m, sh, $NP(C_{20}H_{12}O_2Br_2)$), −6.6 (s, ($OC_6H_4PPh_2$)), −21.8 (m, [$NP(OC_6H_4PPh_2)_2$]).

$\{[NP[O_2C_{20}H_{10}(SiR_1R_2R_3)_2]]_{0.8}][NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ [$R_1R_2R_3$ = Me_3 (III), $R_1R_2R_3$ = Me_2Ph (IV), $R_1R_2R_3$ = $MePh_2$ (V), $R_1R_2R_3$ = Ph_3 (VI)]. The following procedure corresponds to polymer **III**, the others were made similarly with the amounts and observations indicated in Table 2.

To a solution of **I** (0.5 g, 0.98 mmol, 1.56 mmol of Br) in THF (50 mL) that was cooled at −78 °C was slowly added (1 drop per second) ^{t}BuLi (3.12 mmol; 1.85 mL of a 1.7 M solution in pentane) to give a turbid greenish solution. After the solution was stirred for 1.5 h, $ClSiMe_3$ (3.75 mmol, 0.48 mL) was added at −78 °C and the mixture was allowed to reach room temperature with stirring. Stirring was continued overnight and water (100 mL) was added to give a yellow precipitate that was filtered and washed with methanol. The product was dissolved in THF (30−40 mL), and the solution was concentrated to a viscous liquid that was precipitated by pouring dropwise over methanol (200 mL) with stirring. The precipitate was recovered by filtration and dried in vacuo at room temperature for 1 day to give a yellow solid. Yield: 0.41 g (85%). The polymer was then freed of $P(O)Ph_2$ groups as described below.

To a solution of polymer **III** (0.21 g, 0.42 mmol, 0.17 mmol of $P(O)PPh_2$) in a deoxygenated 1:1 (v:v) THF/toluene mixture (6 mL), PPh_3 (0.09 g, 0.34 mmol) and $HSiCl_3$ (0.67 mL, 6.72 mmol) were added and the mixture was heated at 100 °C overnight. Cold deoxygenated methanol (0 °C) was added (ca. 50 mL) to give a yellow precipitate. The mixture was stirred with solid K_2CO_3 and filtered. The resulting solid was washed with H_2O (3 × 40 mL) and MeOH (3 × 40 mL) (both deoxygenated), and dried in vacuo at room temperature for 1 day to give **III** as a yellow solid (0.19 g, 90% yield).

Polymer III. Anal. Calcd for $C_{28}H_{28}NO_2P_{1.4}Si_{1.6}$ (498.83): C, 67.4; H, 5.66; N, 2.81. Found: C, 63.1; H, 5.42; N, 2.74.

IR spectrum (cm^{-1}, KBr pellets): 3061 w, 3018 w (ν_{CH} arom), 2954 m, 2897 w (ν_{CH} CH_3, $SiMe_3$), 1615 w, 1587 w, 1492 m, 1462 w, 1435 w, 1399 w, 1371 w ($\nu_{C=C}$ aromatic rings), 1319 (m, ν_{C-OP}), 1249 sh, 1217 vs, 1168 sh (ν_{NP}), 1134 w, 1111 m (Si-arom), 1068 (m, ν_{P-OC}), 967 (s, δ_{POC}), 905 s, 839 s (methyl rocking), 774 w, 751 m (methyl rocking), 696 w, 663 w, 624 w, 600 w, 575 (m, δ_{NPO}), 548 w, 494 w, 475 w.

^1H NMR ($CDCl_3$, 25 °C): δ = 5−9 (very br m, aromatic rings, centered at δ = 6.8); 1.2 to −1.0 (br, Methyl groups; centered at δ = 0.2). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): −2.9 (m, br $NP(C_{20}H_{12}O_2\{SiMe_3\}_2)$), −6.8 (s, ($OC_6H_4PPh_2$)), −21 (m, br, [$NP(OC_6H_4PPh_2)_2$]).

TGA: weight loss centered at 445 °C (−57%); residue at 800 °C (26%).

Polymer IV. Anal. Calcd for $C_{36}H_{31.2}NO_2P_{1.4}Si_{1.6}$ (598.14): C, 72.3; H, 5.26; N, 2.34. Found: C, 69.4; H, 5.09; N, 2.58.

IR spectrum (cm^{-1}, KBr pellets): 3061 w, 3018 w (ν_{CH} arom), 2952 m, 2903 w (ν_{CH} CH_3, Si−Me_2), 1612 w, 1587 w, 1489 w, 1461 w, 1427 (w, $\nu_{C=C}$ aryl groups), 1403 w, 1371 w, 1318 m (ν_{C-OP}), 1243 sh, 1213 vs, 1167 sh (ν_{NP}), 1110 m (Si-arom), 1067 m (ν_{P-OC}), 965 m (δ_{POC}), 901 w, 830 m (methyl rocking), 807 s, (δ_{PNP}, methyl rocking), 774 m, 729 m, 697 m (monosubstituted phenyl), 662 w, 574 w (δ_{NPO}), 548 w, 469 m.

^1H NMR ($CDCl_3$, 25 °C): δ = 5−10 (very br m, aromatic rings; centered at δ = 7.2); +2.5 to −1.5 (br, methyl groups; centered at δ = 0.3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, 25 °C): −2.2 (m, br $NP(C_{20}H_{12}O_2\{SiMe_2Ph\}_2)$), −6.8 (s, ($OC_6H_4PPh_2$)), −20 (m, br, [$NP(OC_6H_4PPh_2)_2$]).

TGA: weight loss centered at 477 °C (−44%); residue at 800 °C (49%).

Polymer V. Anal. Calcd for $C_{44}H_{34.4}NO_2P_{1.4}Si_{1.6}$ (697.45): C, 75.8; H, 5.00; N, 2.01. Found: C, 70.0; H, 4.78; N, 2.57.

IR spectrum (cm^{-1}, KBr pellets): 3067 m, 3048 m, 3020 d (ν_{CH} arom), 2957 d, 2835 d (ν_{CH} CH_3, Si−Me), 1613 w, 1588 w, 1489 w, 1462 w, 1428 (m, $\nu_{C=C}$ aryl groups), 1372 w, 1318 m (ν_{C-OP}), 1253 sh, 1217 vs, 1168 sh (ν_{P-OC}), 1111 m (Si-arom), 1069 m (ν_{P-OC}), 965 m (δ_{POC}), 901 w, 836 m, 809 m, (δ_{PNP}) 782 m (methyl rocking), 736 m, 698 m (monosubstituted phenyl), 664 w, 576 w (δ_{NPO}), 550 w, 480 m.

TGA: Two weight losses at 451 °C (−51%) and 709 °C (25%); residue at 800 °C (20%).

Polymer VI. Anal. Calcd for $C_{52}H_{37.6}NO_2P_{1.4}Si_{1.6}$ (796.76): C, 78.4; H, 4.76; N, 1.8. Found: C, 68.2; H, 3.8; N, 2.0.

IR spectrum (cm^{-1}, KBr pellets): 3067 m, 3048 m (ν_{CH} arom), 1614 w, 1589 w, 1491 w, 1461 w, 1428 (m, $\nu_{C=C}$ aryl groups), 1376 w, 1318 m (ν_{C-OP}), 1253 sh, 1218 vs, 1172 sh (ν_{P-OC}), 1108 m (Si-arom), 1070 m (ν_{P-OC}), 964 m (δ_{POC}), 893 w, 865 w, 830 w, 812 m, (δ_{PNP}) 743 m, 699 m (monosubstituted phenyl), 664 w, 571 w (δ_{NPO}), 513 m, 496 m.

TGA: Weight loss centered at 468 °C (−42%); residue at 800 °C (48%).

Conclusions

A simple route to directly functionalize binaphthoxyphosphazene units has been used to obtain new optically active

polyphosphazenes $\{[NP(O_2C_{20}H_{10}\{SiR_1R_2R_3\}_2)]_{0.8}[NP(OC_6H_4PPh_2)_2]_{0.2}\}_n$ with silyl groups in the 6,6′-binaphthyl positions. In addition these polymers contain phosphine ligands completely free of oxidized sites that are inside sterically demanding chiral environments. The method to convert $P(O)Ph_2$ in PPh_2 groups utilizing $SiMeCl_3$ and PPh_3 has been successfully adapted to be used at the high molecular weight level.

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