Synthesis of New Phosphazene High Molecular Weight Polymers Containing Functionalized and Optically Active Spirocyclic Groups

Gabino A. Carriedo,* Francisco J. García Alonso, Pedro A. González, and José L. García-Alvarez

Departamento de Química Orgánica e Inorgánica, Facultad de Química, Universidad de Oviedo, Oviedo 33071 Spain

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ABSTRACT: The polymer $[NPCl_2]_n$ reacts with the functionalized biphenols bis(2-hydroxy-5-chlorophenyl)-methane $[(HOC_6H_3Cl)_2CH_2]$, bis(2-hydroxyphenyl) ketone $[(HOC_6H_4)_2CO]$, and [racemic(±)]-, [*R*(+)]-, or [*S*(−)]-1,1′-binaphthyl-2-ol $[(HOC_{10}H_6C_{10}H_6OH)]$ (binaphthol), in THF, or 1,4-dioxane in the presence of K_2CO_3 or Cs_2CO_3 to give respectively the spirocyclic phosphazene homopolymers $[NP(O_2C_{13}H_8Cl_2)]_n$ (**1**), $[NP(O_3C_{13}H_8)]_n$ (**2**), (±)-$[NP(O_2C_{20}H_{12})]_n$ (**5**), (−)-$[NP(O_2C_{20}H_{12})]_n$ [(−)-**5b**], and (+)-$[NP(O_2C_{20}H_{12})]_n$ [(+)-**5b**], some of them also obtained as blends with poly(tetrahydrofuran). The reaction of $[NPCl_2]_n$ first with $(HOC_6H_3Cl)_2CH_2$ or $(HOC_6H_4)_2CO$ and subsequently with 2,2′-biphenol ($(HO)C_6H_4C_6H_4(OH)$) in THF and in the presence of K_2CO_3 gave the random mixed copolymers $[NP(O_2C_{12}H_8)_{0.6}(O_2C_{13}H_8Cl_2)_{0.4}]_n$ (**3**) and $[NP(O_2C_{12}H_8)_{0.6}(O_3C_{13}H_8)_{0.4}]_n$ (**4**). For comparison with the polymers, the two cyclic enantiomers (+)-$[N_3P_3(O_2C_{20}H_{12})_3]$ [(+)-**6**] and (−)-$[N_3P_3(O_2C_{20}H_{12})_3]$ [(−)-**6**] have been prepared from $[N_3P_3Cl_6]$ and [*S*(−)]- or [*R*(+)]-binaphthol, respectively, in acetone in the presence of Cs_2CO_3.

Introduction

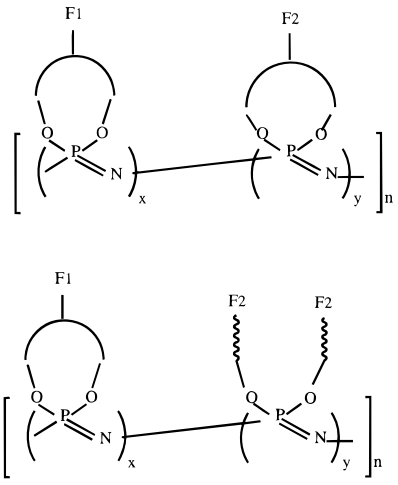
Polyphosphazenes are a very important class of inorganic polymers.[1] Earlier, we reported[2] that the poly(dichlorophosphazene) $[NPCl_2]_n$, as prepared by the polymerization of $[N_3P_3Cl_6]$ in solution promoted by sulfamic acid, described by Magill et al.,[3] reacts directly with 2,2′-$(HO)C_6H_4C_6H_4(OH)$ in THF and K_2CO_3, affording a new type of phosphazene high molecular weight polymer containing 2,2′-dioxybiphenyl groups and having variable amounts of poly(tetrahydrofuran) (PTHF) $[NP(O_2C_{12}H_8)\cdot x(OC_4H_8)]_n$ (i in Scheme 1). Later we found that those materials are strongly interacting blends and that the homopolymer $[NP(O_2C_{12}H_8)]_n$ can be obtained free of PTHF by using 1,4-dioxane as solvent.[4] Other types of "spirocyclic polyphosphazenes", having lower molecular weights, have been also obtained by a condensation reaction.[5]

The results reported herein show that the case of 2,2′-$(HO)C_6H_4C_6H_4(OH)$ is not an exception. We have found that other aromatic diols can also form un-cross-linked products in their direct reaction with $[NPCl_2]_n$ in the presence of K_2CO_3, or, in some cases, using Cs_2CO_3 as proton abstractor,[6] leading to new spirocyclic polyphosphazenes. Furthermore, using [*S*(−)]- or [*R*(+)]-1,1′-binaphthyl-2-ol $(HOC_{10}H_6C_{10}H_6OH)$ (binaphthol) we have prepared a new type of chiral polymeric phosphazene.

This result opens a route to new functionalized phosphazene polymers of the general type depicted in Chart 1 that can combine chemical reactivity with enantiomeric induction. In particular, the presence of binaphthyl units in a polymer is very interesting.[7] Some recent uses include the making of materials for host−guest interactions useful in enantiomeric separations,[8] catalysis,[9] or the incorporation of chirality in LB films.[10]

* E-mail: gac@sauron.quimica.uniovi.es.

Chart 1



Experimental Section

Materials. All the reactions were carried out under dry nitrogen.

K_2CO_3 and Cs_2CO_3 were dried at 140 °C prior to use. The acetone used as solvent was predistilled from $KMnO_4$ and distilled twice from anhydrous $CaSO_4$. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. 1,4-Dioxane was distilled from Na in the presence of benzophenone. Petroleum ether refers to that fraction with boiling point in the range 60−65 °C. The diphenols $(HOC_6H_3Cl)_2CH_2$ (95% purity) and $(HOC_6H_4)_2CO$ (98% purity) were used as purchased (Aldrich), while the (+)- and (−)-binaphthols[11] were prepared as described in the literature. For the reactions we used products having $[\alpha]_D$ of +33.2 or −33.2 (at $c = 1$ in THF), respectively. The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Fluka) was purified from hot petroleum ether and dried in a vacuum. The starting polymer $[NPCl_2]_n$ was prepared by heating the melted $[N_3P_3Cl_6]$, as described by Allcock et al.,[12] or by the polymerization reaction in solution described by Magill et al.[3] Hereafter, we shall refer to these two different starting poly(dichlorophosphazenes) as MEL-PDP or SLN-PDP, respectively.

Measurements. The IR spectra were recorded with Perkin-Elmer FT 1720-X and Paragon 1000 spectrometers. NMR

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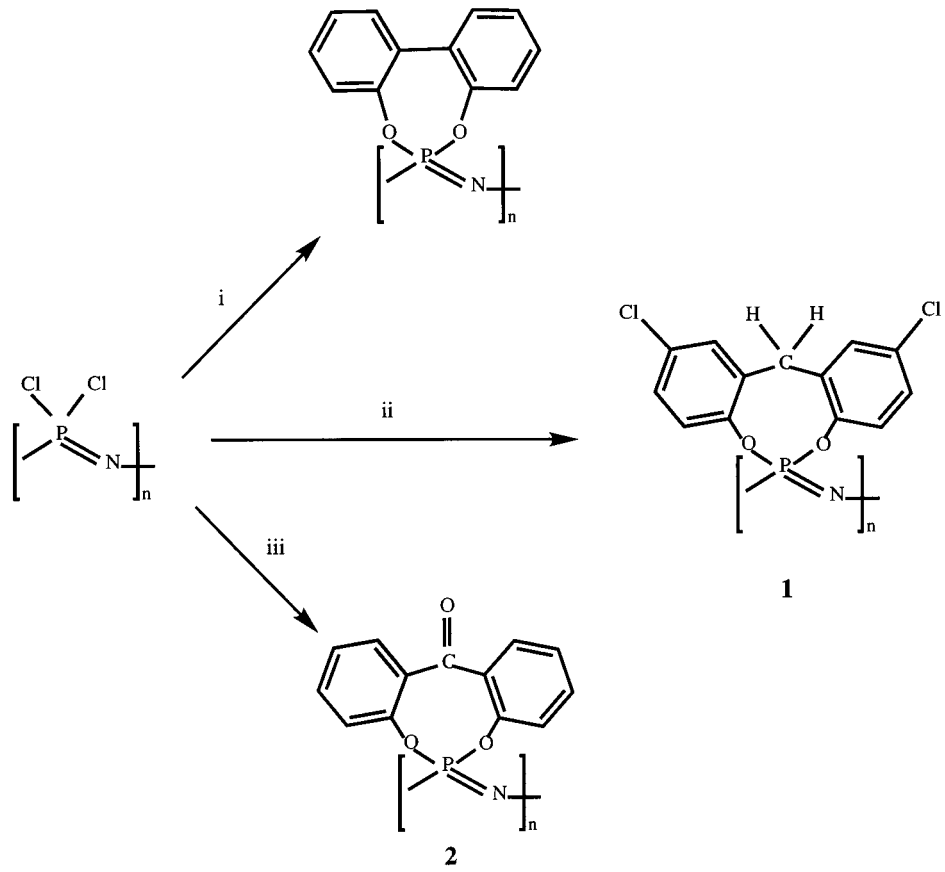
Scheme 1[a]



[a] i. $(HOC_6H_4)_2$ with K_2CO_3 in THF. ii. $(HOC_6H_3Cl)_2CH_2$ with K_2CO_3 in THF. iii. $(HOC_6H_4)_2CO/K_2CO_3$/THF.

spectra were recorded on Bruker AC-200 and AC-300 instruments, using $CDCl_3$ as solvent unless otherwise stated. ^1H and $^{13}C\{^1H\}$ NMR are given in δ relative to tetramethylsilane (TMS). $^{31}P\{^1H\}$ NMR are given in δ relative to external 85% aqueous H_3PO_4. Coupling constants are in hertz. C, H, N analyses were performed with a Perkin-Elmer 2400 microanalyzer. The chlorine analyses were performed by Galbraith Laboratories. Gel permeation chromatograms (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 calibrations 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, at 10 °C/min. Thermal gravimetric analyses (TGA) were performed on a Mettler TA 4000 instrument. The polymer samples were heated at a rate of 10 °C/min from ambient temperature to 800 °C under a constant flow of nitrogen. The specific optical rotation $[\alpha]_D$ was measured with a Perkin-Elmer 241 polarimeter, near 25 °C in $CHCl_3$ (or THF) solution at $c = 1$ unless otherwise stated, checking all the times that the value for (−)-cinchonidine in ethanol was in the range 106 ± 3° at $c = 1.5$.

Synthesis of the Polyphosphazenes. $\{NP(O_2C_{13}H_8Cl_2)\cdot 0.35(OC_4H_8)\}_n$ (1a). To a solution of $[NPCl_2]_n$ (SLN-PDP) (2.3 g, 19.85 mmol) in THF (220 mL) were added $(HOC_6H_3Cl)_2CH_2$ (8.01 g, 29.76 mmol) and K_2CO_3 (10.97 g, 79.38 mmol), and the mixture was refluxed for 65 h with vigorous mechanical stirring. The mixture was poured into water (1.5 L) to give a white precipitate that was washed twice with water (1.5 L) and dissolved in THF (200 mL). The solution was filtered and concentrated to a viscous liquid that was poured dropwise into water (1.5 L) with stirring. The product was similarly reprecipitated once from THF/2-propanol, and once from THF/petroleum ether. The resulting white solid was predried first in a vacuum at room temperature and then at 70 °C for 7 days. The product was $\{NP(O_2C_{13}H_8Cl_2)\cdot 0.35(OC_4H_8)\}_n$ (7.5% THF in weight). Yield: 4.7 g, 70%. ^1H NMR (acetone-d_6 or THF-d_8): δ 5.5−8.5 very broad (m, 6H, aromatic rings), 3.4 (m), 1.6 (m) (2.8H, PTHF). $^{31}P\{^1H\}$ NMR (acetone-d_6): −16.5 (very broad); (THF/D_2O) −17.7 (very broad). $^{13}C\{^1H\}$ NMR (acetone-d_6): 120−154 (broad) (aromatic ring), 71.4, 27.8 (PTHF). Anal. Calcd for $C_{14.4}H_{10.8}O_{2.35}NPCl_2$: C, 51.3; H, 3.23; N, 4.14; Cl, 21.0. Found: C, 50.9; H, 3.17; N, 3.96; Cl, 21.0. M_w (GPC): 2 100 000 ($M_w/M_n = 2.3$). TGA: −7.4% (350 °C), −43% (480 °C). Residue at 800 °C: 40%. T_g(DSC): not observable.

$[NP(O_2C_{13}H_8Cl_2)]_n$ (1b) and (1c). To a solution of $[NPCl_2]_n$ (SLN-PDP) (2.2 g, 18.98 mmol) in 1,4-dioxane (215 mL) were added $(HOC_6H_3Cl)_2CH_2$ (7.66 g, 28.47 mmol) and K_2CO_3 (10.5 g, 75.97 mmol), and the mixture was refluxed for 176 h with vigorous mechanical stirring. After that, polymer **1b** was isolated and purified following the same procedure as that for **1a**. Yield: 3.9 g, 66%. Anal. Calcd for $C_{13}H_8O_2NPCl_2$: C, 50.0; H, 2.58; N, 4.49; Cl, 22.7. Found: C, 50.1; H, 2.65; N, 3.90; Cl, 21.0. M_w(GPC): 1 700 000 ($M_w/M_n = 5.1$). TGA: −42% (480 °C). Residue at 800 °C: 48%. T_g(DSC): 220 °C with ΔC_p of 0.11 J g^{-1} K^{-1}.

The same procedure as for **1b** but using MEL-PDP (1.94 g, 16.74 mmol) in THF (200 mL), $(HOC_6H_3Cl)_2CH_2$ (6.76 g, 25.11 mmol), and K_2CO_3 (9.25 g, 66.96 mmol) (reaction time 87 h) gave **1c**. Yield: 4.0 g, 77%. Anal. Calcd for $C_{13}H_8O_2NPCl_2$: C, 50.0; H, 2.58; N, 4.49; Cl, 22.7. Found: C, 50.1; H, 2.40; N, 4.40; Cl, 18.3. M_w(GPC): 3 200 000 ($M_w/M_n = 5.2$). TGA: −43.2% (480 °C). Residue at 800 °C: 51%. T_g(DSC): 220 °C with ΔC_p of 0.14 J g^{-1} K^{-1}.

$\{NP(O_3C_{13}H_8)\cdot 0.3(OC_4H_8)\}_n$ (2a). To a solution of $[NPCl_2]$ (SLN-PDP) (2.3 g, 19.8 mmol) in THF (250 mL) were added 2,2′-$(HOC_6H_4)_2CO$ (7.5 g, 35.01 mmol) and K_2CO_3 (12.9 g, 93.3 mmol), and the mixture was refluxed for 96 h with vigorous mechanical stirring. After that, polymer **2a** was isolated and

purified following the same procedure as for **1**. The resulting pale yellow solid $\{NP(O_3C_{13}H_8)\cdot 0.3(OC_4H_8)\}_n$ (7.7% PTHF in weight) was predried first in a vacuum at room temperature and then at 70 °C for 7 days. Yield: 2.8 g, 51%. ^{1}H NMR ($CDCl_3$): δ 5.8−8.2 (m, 8 H, aromatic rings), 3.4 (m), 1.6 (m) (2.4H, PTHF). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −12.0 (very broad) (−11.8 in THF/D_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 118−151 (broad) (aromatic rings); 71.3, 27.2 (PTHF). Anal. Calcd for $C_{14.2}H_{10.4}O_{3.3}NP$: C, 61.2; H, 3.76; N, 5.02. Found: C, 58.4; H, 3.63; N, 4.84. Chlorine content: 0.28%. M_w(GPC): 700 000 ($M_w/M_n = 2.4$). TGA: continuous loss from 150 °C. Residue at 800 °C: 60%. T_g(DSC) not observable.

$\{NP(O_3C_{13}H_8)\}_n$ (2b). The same procedure but using $[NPCl_2]_n$ (MEL-PDP) (1.94 g, 16.74 mmol) in THF (200 mL), 2,2′-$(HOC_6H_4)_2CO$ (5.38 g, 25.11 mmol), and K_2CO_3 (9.25 g, 66.93 mmol). Reaction time: 95 h. The yellow product obtained contained only traces of PTHF (0.02 mmol/mmol of $[NP(O_2R)]$ unit). Yield: 3.7 g, 86%. ^{1}H NMR ($CDCl_3$): δ 5.8−8.2 (m, 8 H, aromatic rings).$^{31}P\{^1H\}$ NMR ($CDCl_3$): −12.0 (very broad) (−11.8 in THF/D_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 118−151 (broad). Anal. Calcd for $C_{13}H_8O_3NP$: C, 60.7; H, 3.13; N, 5.44. Found: C, 59.3; H, 3.10; N, 5.20. Chlorine content: 0.16%. M_w(GPC): 500 000 ($M_w/M_n = 2.1$). TGA: continuous loss from 150 °C. Residue at 800 °C: 62.2%. T_g(DSC) not observable.

$[NP(O_2C_{12}H_8)_{0.6}(O_2C_{13}H_8Cl_2)_{0.4}\cdot 0.1(OC_4H_8)]_n$ (3). To a solution of $[NPCl_2]_n$ (SLN-PDP) (1.6 g, 13.81 mmol) in THF (200 mL) were added $(HOC_6H_3Cl)_2CH_2$ (1.24 g, 4.6 mmol) and K_2CO_3 (7.63 g, 55.21 mmol), and the mixture was refluxed for 18 h with vigorous mechanical stirring. Then, the phenol 2,2′-$HOC_6H_4C_6H_4OH$ (6.85 g, 36.79 mmol) was added and refluxing was continued for 95 h. After that, the polymer **3** was isolated and purified following the same procedure as for **1**. The white product contained 2.7% in weight of PTHF. Yield: 2.2 g, 59%.

^{1}H NMR ($CDCl_3$): δ 6.0−8.0 (very broad multiplet, 7.2 H, aromatic rings), 3.4 (m), 1.6 (m) (0.8 H, PTHF). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −4.91 [m, $P(O_2C_{12}H_8)$], −21.4 [m, with another smaller broad peak at −19.0, $P(O_2C_{13}H_8Cl_2)$] (−4.45 and −21.32 in THF). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 123, 126, 129, 135, 148, 149 (broad peaks, aromatic rings), 71.3, 27.2 (PTHF). Anal. Calcd for $C_{12.8}H_{8.8}O_{2.1}NPCl_{0.8}$: C, 57.0; H, 3.29; N, 5.20; Cl, 10.5. Found: C, 56.5; H, 3.19; N, 5.42; Cl, 9.7. M_w(GPC): 1 900 000 ($M_w/M_n = 5.0$). TGA: −6% (350 °C), −42% (490 °C). Residue at 800 °C: 48%. T_g(DSC) 167 °C, with ΔC_p of 0.23 J g^{-1} K^{-1}.

$[NP(O_2C_{12}H_8)_{0.6}(O_3C_{13}H_8)_{0.4}\cdot 0.3(OC_4H_8)]_n$ (4). To a solution of $[NPCl_2]_n$ (SLN-PDP) (2.3 g, 19.85 mmol) in THF (200 mL) were added 2,2′-$(HOC_6H_4)_2CO$ (1.42 g, 6.63 mmol) and K_2CO_3 (10.97 g, 79.4 mmol), and the mixture was refluxed for 15 h with vigorous mechanical stirring. Then, the phenol 2,2′-$HOC_6H_4C_6H_4OH$ (9.86 g, 52.9 mmol) was added and refluxing was continued for 286 h. After that, polymer **4** was isolated and purified following the same procedure as for **1**. The pale yellow product contained 8.2% in weight of PTHF. Yield: 3 g, 58%. ^{1}H NMR ($CDCl_3$): δ 6.0−8.0 (m, 8H, aromatic rings), 3.4 (m), 1.6 (m) (2.4 H, PTHF). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −5.17 [m, $P(O_2C_{12}H_8)$], −14.84 [m, $P(O_3C_{13}H_8)$] (−5.3 and −15.05 in THF/D_2O). $^{13}C\{^1H\}$ NMR ($CDCl_3$): 124, 126, 130, 132, 133, 134, 149, 150 (broad peaks) (aromatic rings), 71.3, 27.2 (PTHF). Anal. Calcd for $C_{13.6}H_{10.4}O_{2.7}NP$: C, 62.3; H, 4.0; N, 5.35. Found: C, 60.0; H, 4.04; N, 5.54. Chlorine content: 0.26%. M_w(GPC) 374 000 ($M_w/M_n = 4.5$). TGA: −8.3% (320 °C), −43% (450 °C). Residue at 800 °C: 42%. T_g(DSC) probably at 157 °C, with ΔC_p of 0.09 J g^{-1} K^{-1}.

(±)-$[NP(O_2C_{20}H_{12})\cdot 0.5(OC_4H_8)]_n$ [(±)5a)]. To a solution of $[NPCl_2]_n$ (SLN-PDP) (1.8 g, 15.5 mmol) in THF (270 mL) were added racemic-$(HO)_2(C_{20}H_{12})$ (6.66 g, 23.3 mmol) and Cs_2CO_3 (20.2 g, 62 mmol), and the mixture was refluxed for 4 h with vigorous mechanical stirring. After that, the white polymer (**5a**) was isolated and purified following the same procedure as for **1**. The resulting slightly yellowish product, contained 9.9% in weight of PTHF and was predried first in a vacuum at room temperature and then at 70 °C for 7 days. Yield: 3.5 g, 62%.

Table 1. Results of the Heating of Polymer [(−)-5b] at 130 °C

time, days	M_w (PDI)	α_D[a]
0	800 000 (2.6)	−196
0.5	600 000 (3.2)	−192
1	500 000 (3.2)	−185
2.5	250 000 (2.8)	−170
5	200 000 (2.8)	−163
10	160 000 (2.6)	−152
15	140 000 (2.5)	−148
30	120 000 (2.5)	*b*

[a] Specific rotation at $c = 1$ in $CHCl_3$, measured near 25 °C. [b] Not well reproducible.

^{1}H NMR ($CDCl_3$): 10−5 very broad with a maximum at ca. 7.2 (m, 12H, aromatic rings), 3.42 (m), 1.62 (m) (4H, PTHF), 1.85−0.8 (m) (hydrocarbons). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −4 (very broad). Anal. Calcd for $C_{22}H_{16}O_{2.5}NP$: C, 72.3; H, 4.40; N, 3.83. Found: C, 72.3; H, 4.58; N, 3.71. Chlorine content: 0.36%. M_w(GPC): 830 000 ($M_w/M_n = 9$). TGA: −10.6% in two steps (350 °C). Residue at 800 °C: 50.4%. DSC: no observable features.

$[NP(O_2C_{20}H_{12})]_n$ [(±)-5b, (−)-5b, and (+)-5b]. To a solution of $[NPCl_2]_n$ (SLN-PDP) (1.43 g, 12.37 mmol) in dioxane (190 mL) were added (+)-$(HO)_2(C_{20}H_{12})$ ($[\alpha]_D = +33.2$) (4.25 g, 14.84 mmol) and Cs_2CO_3 (12.09 g, 37.11 mmol), and the mixture was refluxed for 12 h with vigorous mechanical stirring. The reaction mixture was poured into water to give an off white solid (3.36 g, 82%) that was extracted with THF (0.5 L) overnight and filtered to give a cloudy but transparent solution. This was concentrated at reduced pressure near to precipitation and poured into water. The resulting solid was similarly reprecipitated from THF/2-propanol and THF/hexane. (In case the addition to 2-propanol of the saturated solution in THF does not give a solid, the mixture can be concentrated at reduced pressure until a well-formed precipitate appears.) The resulting white product was predried first in a vacuum at room temperature and then at 70 °C for 30 days to give the slightly yellowish polymer [(−)-**5b**]. Yield: 1.4 g, 34%. The product contained hydrocarbons in variable amounts that depended on the drying time at 70 °C. Thus after 9 days the content (calculated as hexane) was ca. 7.5% in weight, and after 30 days it was 5%. Further reduction was very slow at this temperature.

^{1}H NMR ($CDCl_3$): 10−5 (very broad with a maximum at ca. 7.2) (m, 12 H, aromatic rings), 1.85−0.8 (m) (2.7 H, hydrocarbons). Measured in DMSO-d_6 at 393 K, the protons of the aromatic rings give a multiplet with peaks at 6.76, 6.87, 6.98, 7.2, 7.59, 1.69. $^{31}P\{^1H\}$ NMR ($CDCl_3$): −3 (v broad). Measured in DMSO-d_6 at 393 K it was a sharp peak at −3.5. Anal. Calcd for $C_{20}H_{12}O_2NP$: C, 73.0; H, 3.67; N, 4.25. Found: C, 72.4; H, 4.19; N, 3.85. Chlorine content: 0.2%. M_w(GPC): 800 000 ($M_w/M_n = 2.6$). $[\alpha]^{30}_D = -196$. TGA: −6% (from ca. 100 to ca. 400 °C), −41% (540 °C). Residue at 800 °C: 53%. T_g(DSC) not observable.

Heating the polymer at 130 °C progressively reduced the amount of hydrocarbons to ca. 2%, but the different products obtained at various times, all with the same C, H, N analysis, were darker and had reduced M_w and $[\alpha]_D$ values (see Table 1).

The other isomers were similarly prepared. Relevant data are given below. The M_w, the hydrocarbon content, and the $[\alpha]_D$ varied slightly with the drying time at 70 °C.

[(+)-5b]: dried 7 days. Yield: 30−50%. Ca. 8% in weight of hydrocarbons. Anal. Calcd for $C_{20}H_{12}O_2NP$: C, 73.0; H, 3.67; N, 4.25. Found: C, 72.1; H, 4.21; N, 4.10. Chlorine content: 0.1%.

M_w(GPC): 1 100 000 ($M_w/M_n = 3.6$). $[\alpha]^{30}_D = +209$.

[(±)-5b]: dried 7 days. Yield: 34%. Ca. 6% in weight of hydrocarbons. Anal. Calcd for $C_{20}H_{12}O_2NP$: C, 73.0; H, 3.67; N, 4.25. Found: C, 71.9; H, 3.66; N, 4.12. Chlorine content: 0.2%. M_w(GPC): 800 000 ($M_w/M_n = 4$).

The polymer **$[NP(O_2C_{20}H_{12})]_n$ [(−)-5c]** was similarly obtained using MEL-PDP (0.817 g, 7.05 mmol) and [*R*(+)]-

binaphthol (2.22 g, 7.76 mmol). After the reflux for 12 h the reaction mixture was poured into water and the precipitate was washed with water, acetone, and ether, and dried in a vacuum. This crude product (2.06 g, 86.8%) was not pure (Anal. Found: C, 67.0; H, 3.39; N, 3.82) and was not totally soluble in THF. It was purified by extracting it with chloroform, filtering, and reprecipitating successively from chloroform/2-propanol and chloroform/hexane. The final yield was 0.42 g (18.2%) of a nearly white solid. Anal. Found: C, 72.5; H, 4.00; N, 4.01. Chlorine content: 0.35%. M_w(GPC) 1 100 000 ($M_w/M_n = 9.5$). $[\alpha]^{20}_D = -207$. TGA: −4.4% (from ca. 100 to ca. 400 °C), −42.6% (540 °C). Residue at 800 °C: 53%.

(−)-[$N_3P_3(O_2C_{20}H_{12})_3$] (6a). A mixture of [$N_3P_3Cl_6$] (0.174 g, 0.5 mmol), (*R*)-$(HO)_2(C_{20}H_{12})$ ($[\alpha]_D = +33.2$) (0.473 g, 1.65 mmol), and Cs_2CO_3 (1.47 g, 4.5 mmol) in acetone (40 mL) was refluxed for 4 h with stirring. The volatiles were evaporated in a vacuum, and the residue was washed with water (3 × 50 mL) and ether (3 × 30 mL) and dried in vacuo to give **6a** as a white solid. Yield: 0.28 g (56.2%).

^{1}H NMR ($CDCl_3$): δ 7.9−7.3 (m, 8H, aromatic rings). ^{31}P-{^{1}H} NMR ($CDCl_3$): 27.8. ^{13}C{^{1}H} NMR ($CDCl_3$): 148.1 (broad), 132.9, 132.3, 131.6, 129.1, 127.9, 129.9, 125.9, 122.5, 122.3 (aromatic rings). Anal. Calcd for $C_{60}H_{36}O_6N_3P_3$: C, 73.0; H, 3.67; N, 4.25. Found: C, 71.4; H, 3.49; N, 4.12. $[\alpha]^{25}_D = -64°$ (*c* = 0.5 in $CHCl_3$).

The isomer (+)-[$N_3P_3(O_2C_{20}H_{12})_3$] (**6b**) was similarly prepared from (*S*)-$(HO)_2(C_{20}H_{12})$ ($[\alpha]_D = -33.2$) in 65.3% yield. Anal. Found: C, 71.3; H, 3.52; N, 4.03. $[\alpha]^{25}_D = +68°$ (*c* = 0.5 in $CHCl_3$).

Results and Discussion

The reaction of $[NPCl_2]_n$, prepared by the solution method[3] (or SLN-PDP, see Experimental Section) with bis(2-hydroxy-5-chlorophenyl)methane [$(HOC_6H_3Cl)_2CH_2$] and K_2CO_3 in THF gave the soluble linear polymer $[NP(O_2C_{13}H_8Cl_2)\cdot 0.35(OC_4H_8)]_n$ (**1a**), containing poly(tetrahydrofuran) (PTHF) with a M_w of 2 100 000. In dioxane as solvent the reaction was slower and led to the homopolymer $[NP(O_2C_{13}H_8Cl_2)]_n$ (**1b**) free of PTHF, with a M_w of 1 700 000 (ii in Scheme 1). As observed earlier,[2,4] the analogous reactions of $[NPCl_2]_n$ with 2,2′-biphenol, led to the spirocyclic polyphosphazenes $[NP(O_2C_{12}H_8)\cdot x(OC_4H_8)]_n$ and $[NP(O_2C_{12}H_8)]_n$, respectively, with M_w of the order of 500 000 or less. Therefore, it appears that the thermal degradation of the chains during the substitution reactions with the diol bis(2-hydroxy-5-chlorophenyl)methane is less pronounced than with the 2,2′-biphenol.

The use of $[NPCl_2]_n$ obtained by the melting method[12] (MEL-PDP) and THF as solvent gave the homopolymer $[NP(O_2C_{13}H_8Cl_2)]_n$ (**1c**), also free of PTHF. In this case, the substitution of all the chlorines took more time, and the molecular weight of the product (3 200 000) was higher. In fact, the molecular weights of (aryloxy)phosphazenes prepared from SLN-PDP[3] are lower than those prepared from MEL-PDP.[12]

The reaction of SLN-PDP with the biphenol bis(2-hydroxyphenyl) ketone [$(HOC_6H_4)_2CO$] and K_2CO_3 using THF as solvent was also successful, affording after 100 h the polymer $[NP(O_3C_{13}H_8)\cdot 0.3(OC_4H_8)]_n$ (**2a**) in good yields and with low residual chlorine (0.28%) (iii in Scheme 1). The M_w was 700 000. Using dioxane as solvent, to avoid the PTHF, the resulting polymers had low molecular weights that decreased rapidly with the refluxing time (140 000 for 50 h and 65 000 for 180 h), suggesting that the thermal degradation of the polymeric chains occurs readily. In principle, this could be useful, as polyphosphazenes with low M_w may have some advantages for certain possible applications,[13] but the materials obtained were fine powders that were difficult to handle, and the yields were poor (20−30%). Therefore, we prepared the homopolymer $[NP(O_3C_{13}H_8)]_n$ (**2b**) in THF as solvent but using MEL-PDP. Surprisingly, the molecular weight (500 000) was slightly lower than that of **2a**, even after the same reaction time, which contrasts with that observed for the biphenol $(HOC_6H_3Cl)_2CH_2$.

Taking into account that the biphenols used in the reactions of Scheme 1 are rather bulky, these chlorine substitutions to give un-cross-linked products are surprisingly efficient. This is especially so in the case of $(HOC_6H_3Cl)_2CH_2$, where the rotation around the $-CH_2$ group may induce it to react by only one of the two active HO− groups.[14] However, the same technique also allowed the preparation of the random copolymers with two different cyclic dioxybiphenyl groups shown in Scheme 2.

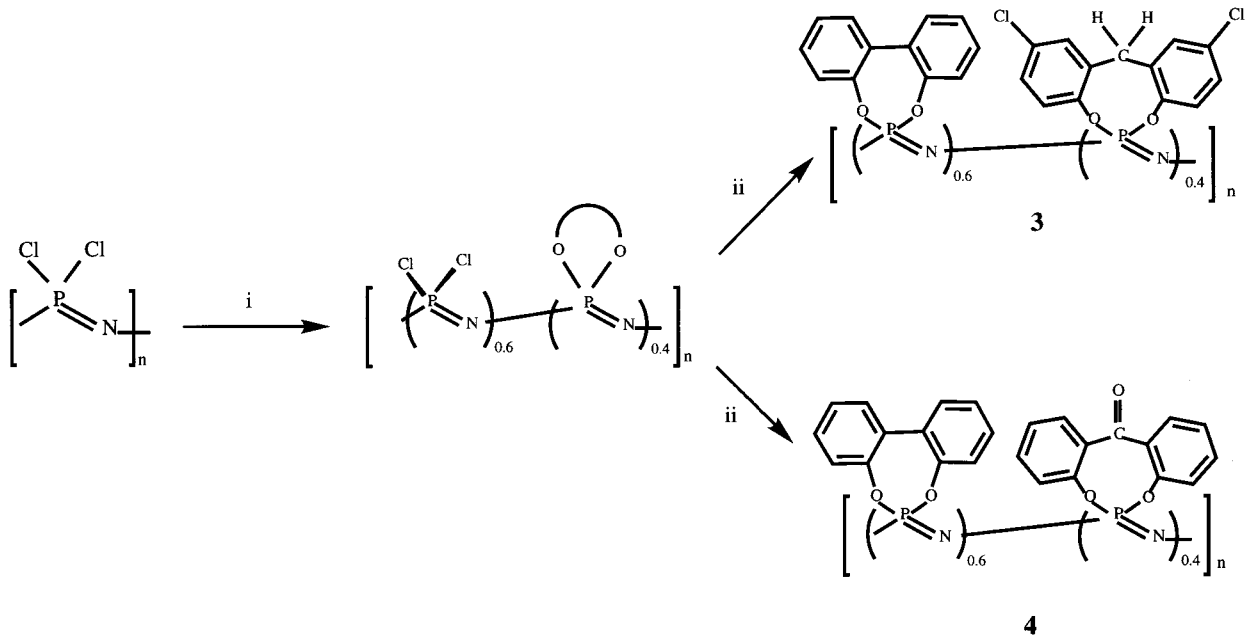
Thus, the reaction of SLN-PDP in THF and K_2CO_3, first with $(HOC_6H_3Cl)_2CH_2$ or $(HOC_6H_4)_2CO$ and subsequently with 2,2′-$(HO)C_6H_4C_6H_4(OH)$ gave the phosphazene polymers $[NP(O_2C_{12}H_8)_{0.6}(O_2C_{13}H_8Cl_2)_{0.4}\cdot 0.1(OC_4H_8)]_n$ (**3**) and $[NP(O_2C_{12}H_8)_{0.6}(O_3C_{13}H_8)_{0.4}\cdot 0.3(OC_4H_8)]_n$ (**4**) (see Scheme 2), obtained with PTHF. In both cases, the second step required much longer refluxing times than the formation of the 2,2′-biphenol homopolymer $[NP(O_2C_{12}H_8)]$, and consistently with the results above, the bis(2-hydroxy-5-chlorophenyl)methane derivative **3** had a much higher M_w (1 900 000) than the bis(2-hydroxyphenyl) ketone polymer **4** (370 000).

All the spectroscopic and analytical data for the new polymers (Experimental Section) were in accord with the formulation proposed. Significantly, the IR spectra did not show signals of −OH groups, indicating the absence of monodentated biphenols. The signals in the ^{31}P NMR spectra taken at room temperature were broad, especially in the case of the $O_2C_{13}H_8Cl_2$ derivatives that were very broad. However, at higher temperatures, the spectra were much sharper (see later). The chemical shifts changed accordingly with the well-known ring-deshielding effects.[15] Thus, in the polymer $[NP(O_2C_{12}H_8)]_n$, where the P atoms are in seven-membered rings, the value is −6 ppm, while in **1** and **2**, with less deshielding eight-membered rings, the value drops to near −15. In the diphenoxyphosphazene where the P atoms are not in rings, the chemical shift is −20. However, in the case of **3**, the signal corresponding to the $NP(O_2C_{13}H_8Cl_2)$ units was very broad and also asymmetric, with two maxima, one at −19 ppm and a much higher one at −21, with a pattern that remained the same in polymers that were prepared with longer reaction times. This might indicate the presence of some unsubstituted $NPCl_2$ groups (expected near −21 ppm), but although this cannot be completely ruled out, it is not consistent with the analytical data (see Experimental Section) and with the solubility and stability of the materials. In fact, taking into account all the possible environments of the P atoms along the polymeric chain in **3**, the presence of signals beetwen −17 (as in **1**) and −21 (the higher maximum in **3**) in its ^{31}P NMR spectrum may be not so surprising.

Although the ^{1}H and ^{13}C NMR spectra were also very broad at room temperature, they showed the expected signals. Only those of the CH_2 group of the $NP(O_2C_{13}H_8Cl_2)$ derivatives (expected near 4 ppm) were not clearly observed.

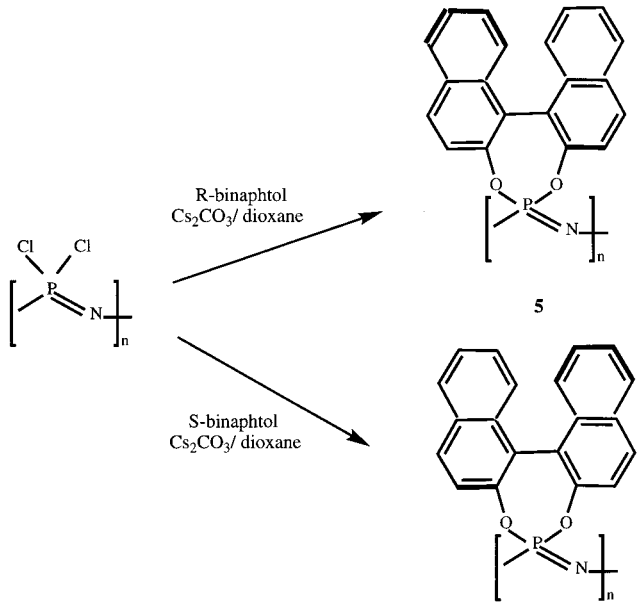
As shown elsewhere,[4] the PTHF-containing polymers are polymer blends that cannot be separated by re-

Scheme 2[a]



[a] i. $(HOC_6H_3Cl)_2CH_2$ or $(HOC_6H_4)_2CO$ with K_2CO_3 in THF. ii. $(HOC_6H_4)_2$ with K_2CO_3 in THF.

Scheme 3



peated reprecipitations from THF/2-propanol even though the PTHF is relatively soluble, suggesting a high degree of interaction between the two components.

Similarly to the 2,2′-biphenol, the 2,2′-binaphthol ($HOC_{10}H_6C_{10}H_6OH$), reacted with $[NPCl_2]_n$ in THF or dioxane, in the presence of K_2CO_3 to give the analogous spirocyclic polyphosphazenes **5** shown in Scheme 3. Although with potassium carbonate the times required to complete the substitution reaction were rather long, the synthesis could be accomplished very easily in a few hours using Cs_2CO_3 as proton abstractor.[6] Thus, with the SLN-PDP in THF the racemic binaphthol gave in only 4 h the soluble PTHF-containing polymer (±)-$[NP(O_2C_{20}H_{12})\cdot 0.5(C_4H_8)]_n$ **[(±)-5a]** having a M_w of 800 000 and 0.36% of unreacted chlorine. In dioxane as solvent, the reaction time was longer, and the product $[NP(O_2C_{20}H_{12})]_n$ **[(±)-5b]** was slightly less soluble, having M_w of 800 000 and much less chlorine.

Using SLN-PDP and the enantiomer [*R*(+)]-$(HO)_2(C_{20}H_{12})$ ($[\alpha]_D^{30} = +33.2$ in THF) in dioxane as solvent, we obtained the optically active phosphazene polymer $[NP(O_2C_{20}H_{12})]_n$ **[(−)-5b]**, although in low yield (34%). The M_w was 800 000 ($M_w/M_n = 2.6$), and the $[\alpha]_D$ was −196 ($c = 1$ in $CHCl_3$), opposite and much higher than that of the starting (+)-binaphthol in THF. However, we observed that, measured in $CHCl_3$, the value for the latter was −4.4. Therefore, in this solvent, the $[\alpha]_D$ of the polymer **[(−)-5b]** has the same sign as the binaphthol, but the value is still much higher.

The preparation of the binaphthoxy polymer using the MEL-PDP afforded the less soluble material $[NP(O_2C_{20}H_{12})]_n$ **[(−)-5c]** in 18% yield (see Experimental Section). The M_w of the fraction that could be extracted with $CHCl_3$ was 1 100 000 with a higher polydispersity index (9.5), and the $[\alpha]_D$ was −207 (in $CHCl_3$).

The same results were obtained with the *S*(−) enantiomer of the binaphthol ($[\alpha]_D = -33.2$ in THF and +5 in $CHCl_3$); that with SLN-PDP gave the polymer (+)-$[NP(O_2C_{20}H_{12})]_n$ **[(+)-5b]** in yields on the order of 45%. The M_w were around 1 100 000, with $[\alpha]_D = +209$ at $c = 1$ in $CHCl_3$.

The relatively low yields obtained for the binaphthoxy polymers may be due to their low solubility, which prevents the complete dissolution necessary for their purification. In fact, all the concentrated solutions in THF are cloudy liquids, although transparent, suggesting the presence of very small particles in suspension. However, it may also indicate that the reaction of the binaphthol with the dichlorophosphazene to give the linear un-cross-linked polymer is not completely efficient, having other secondary processes.

In accord with the proposed structure for **5**, the ^{31}P NMR chemical shift was −3 ppm (see above). The signal was again very broad at room temperature, easily seen in $CDCl_3$ but not in DMSO. However, the heating of the samples in the latter solvent resulted in a conspicuous sharpening of the spectrum (see Figure 1). A very weak peak that appeared near 0 ppm in the spectrum at 120 °C indicated that the polymer under-

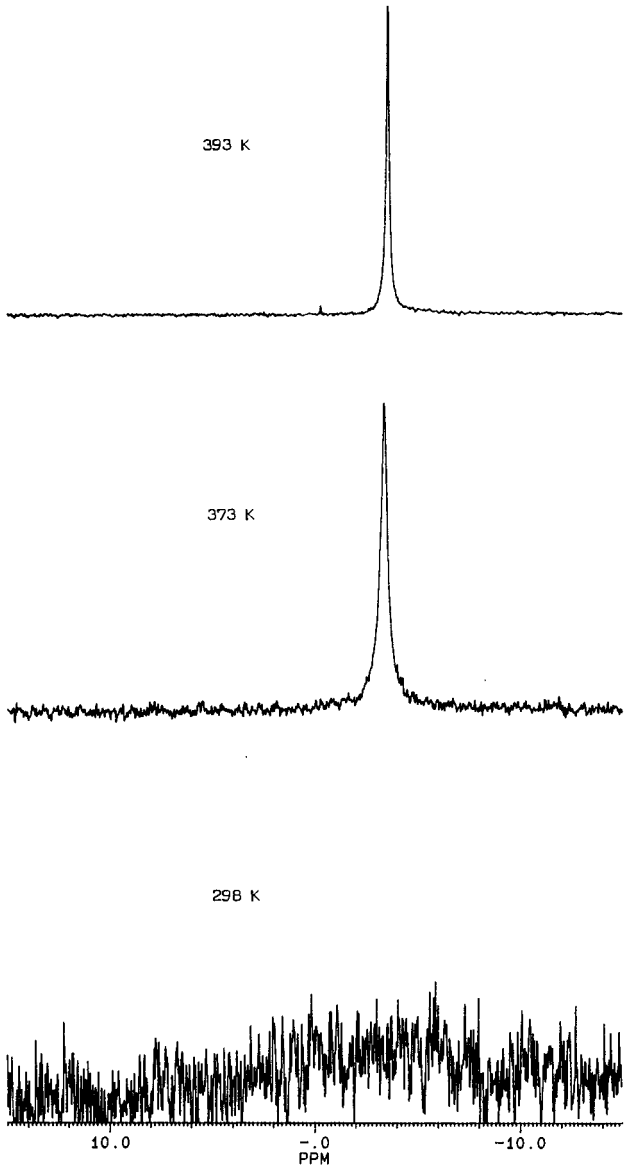


Figure 1. ^{31}P NMR spectrum of polymer **[(−)-5b]** in DMSO-d_6 at various temperatures.

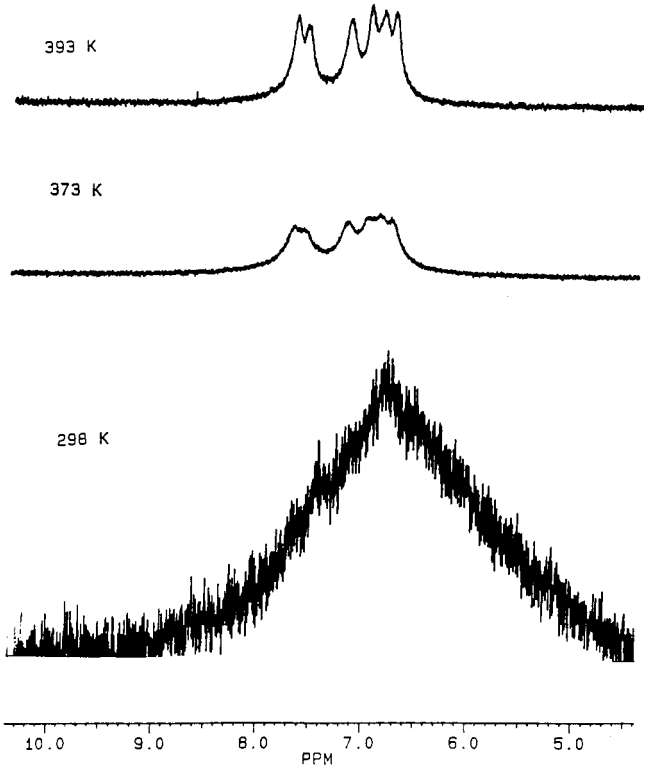


Figure 2. ^{1}H NMR spectrum (aromatic ring region) of polymer **[(−)-5b]** in DMSO-d_6 at various temperatures.

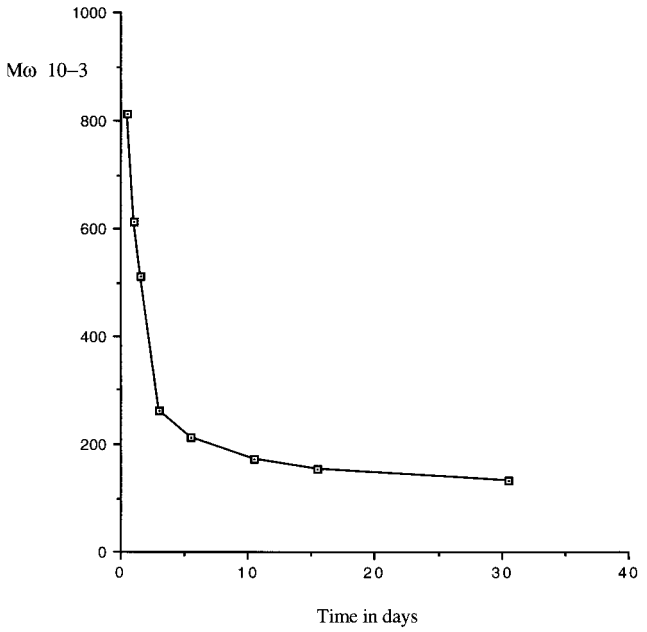


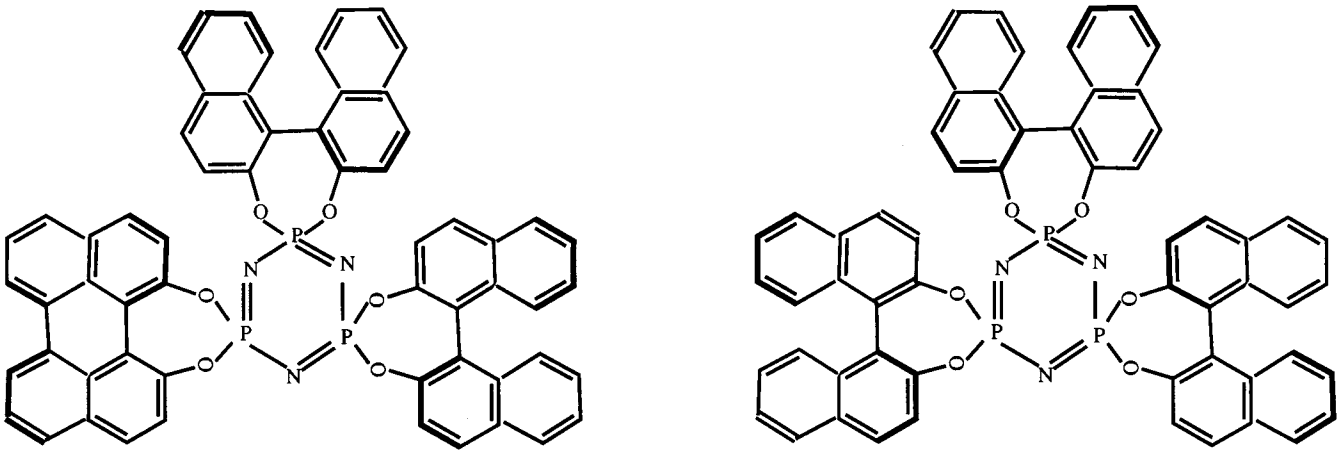
Figure 3. M_w of the polymer **[(−)-5b]** vs the heating time (in days) at 130 °C.

goes a chain degradation on heating, also shown by the decrease in M_w (see later). The ^{1}H NMR spectra were also extremely broad at room temperature, with the signal of the aromatic rings extending from 10 to 4 ppm. However, when the spectra were taken in DMSO at 120 °C, a relatively well-resolved multiplet could be observed (Figure 2). The broad NMR spectra and their temperature dependence suggest that the polymeric chains are fairly rigid, which is in accord with the very high T_g values (see later).

The ^{1}H NMR spectra also showed the presence of some hydrocarbons retained by the polymer in the last precipitation step (see Experimental Section). Drying at 70 °C in a vacuum, accompanied by a slight darkening of the products, reduced these impurities to less than 5% in weight, but they could only be further reduced at higher temperatures. At 130 °C the hydrocarbon content dropped to less than 2%, but the products were yellow to brown, were more soluble, and had lower M_w and $[\alpha]_D$ values (see Table 1). All these data indicate an extended thermal degradation of the polymeric chains, which, according to Figure 3, is very fast at the beginning. The difficulty in obtaining the solvent free polymers is more difficult to explain, but it could be due to the formation of cavities within the solid that can trap and retain efficiently the hydrocarbon molecules.

Although, because of the hydrocarbon content, the specific rotations $[\alpha]_D$ measured for the enantiomeric polymers **5b** have to be taken with caution, the high values observed are clearly in accord with their formulation as polymers containing a chiral repeating unit. Thus, polyphosphazenes with single-carbon chiral centers attached to the main chain by long spacers, have $[\alpha]_D$ values very close to those of the independent starting alcohols,[16] while the polymers containing bi-

Chart 2



6

naphthyl units have oposite and much higher specific optical rotation than the monomeric counterparts.[17] This increase and inversion of the specific rotation has also been observed, for example, in the radical polymerization of a methacrylamide having an L-leucine methyl ester structure,[18] and in the electropolymerization of certain chiral thiophenes.[19]

On the other hand, taking into account that the optical activity of the 2,2′-binaphthyl units is usually thermally very stable,[20] the data in Table 1 (Figure 4) (obtained using samples from the same batch of polymer and checking the C, H, N analysis before the M_w measurement) evidence the strong dependence of the $[\alpha]_D$ on the M_w. This fact, also found in other recently reported polymers with binaphthyl units,[20] may indicate that the polyphosphazenes **5b** have a secondary structure, probably helicoidal, contributing to the optical rotation. This may also explain their limited solubility and the broadness of the NMR spectra. The generation of a secondary order along the polymeric chains in **5** may not be surprising if the possibility of staking of the repeated binaphthyl groups is taken into account.

To compare the specific rotation of the polymer **5b** with the cyclic trimeric counterparts, we reacted $[N_3P_3Cl_6]$ with the corresponding binaphthols and Cs_2CO_3 in acetone to prepare the tris(spirocyclophosphazene)s (+)- and (−)-$[N_3P_3(O_2C_{20}H_{12})_3]$ **(6)** (Chart 2). Thus, with the [*R*(+)]-biphenol, the product was **[(−)-6]** with $[\alpha]_D = -64$ at $c = 0.5$ in $CHCl_3$ (higher concentrations gave cloudy solutions), while the [*S*(−)]-binaphthol gave **[(+)-6]** with $[\alpha]_D^{20} = +68$ at $c = 0.5$ in $CHCl_3$. Therefore, the effect of increasing the specific rotation on going from the binaphthol to the binaphthoxyphosphazenes is also observed in the cyclic trimers. The possibility of formation of the tris spiro derivatives **6**, although in only moderately good yield, is surprising, because, although spiro-[21] and ansa-(binaphthylenedioxy)cyclophosphazenes[22,23] have been prepared, it is known to be difficult to reach even the dichlorobis[spiro-(binaphthylenedioxy)cyclophosphazene] by direct substitution of chlorines in the cycle $[N_3P_3Cl_6]$.[24]

The thermal properties of the new polymers were studied by TGA and DSC. The TGA curves showed that polymers **1**, **3**, and **4** underwent a strong weight loss that is centered at 480 °C, leaving a residue of the order of 50% at 800 °C. This indicates that, as in other cases reported previously,[25] these phosphazenes become thermally degraded, probably with formation of volatile cyclic oligomers. In the case of the copolymers with PTHF, there is an extra weight loss that begins near 200 °C and is centered at ca. 350 °C that, if not overlapped with the other weight loss, almost matched the PTHF content. However, the ketone derivatives **2** and **4** are the less thermally stable, decomposing quicker and at lower temperatures in a rather complex manner (Figure 5). In fact, those polymers may decompose slowly also at room temperature, as suggested by the differences in the IR spectra measured with freshly prepared samples and after several months. By contrast, the binaphthoxy derivatives **5** were surprisingly stable. The TGA curve (Figure 6) shows a continuous loss, matching the content of the solvent molecules retained in the solids, that decreased markedly in the samples heated at 130 °C, and after a period of stability, they began to decompose quickly at 540 °C, leaving a residue of 50% above 800 °C. Even though the weight loss observed in the TGA curves may depend on the scan rate of the measurements, this behavior resembles that

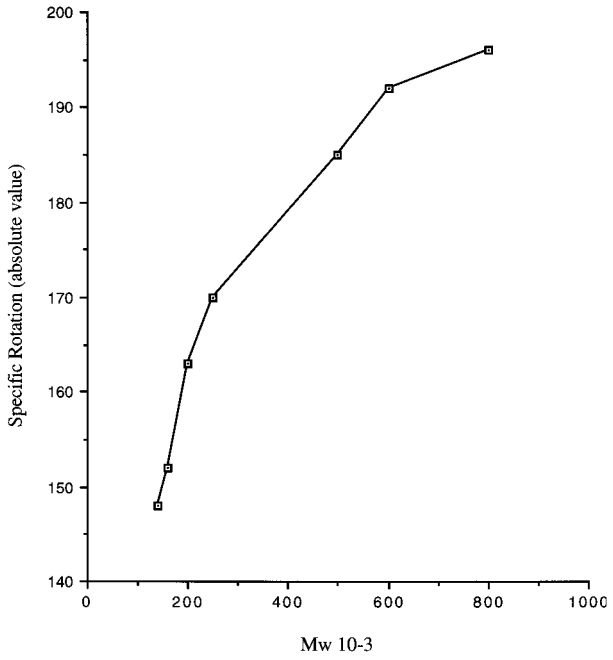


Figure 4. Variation of the specific rotation of **[(−)-5b]** with the M_w.

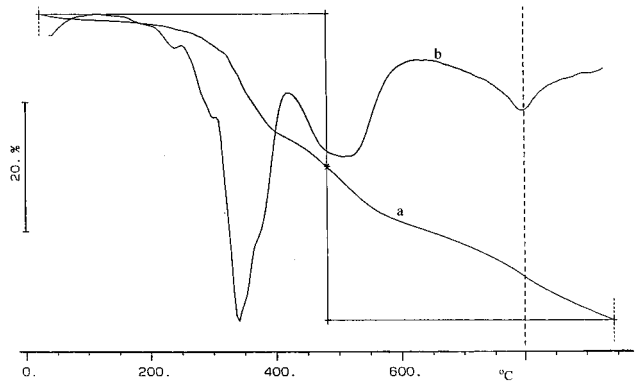


Figure 5. TGA curve of polymer **2** from 20 to 800 °C, heating rate 10 °C/min: (a) weight loss in percent; (b) derivative of the weight loss.

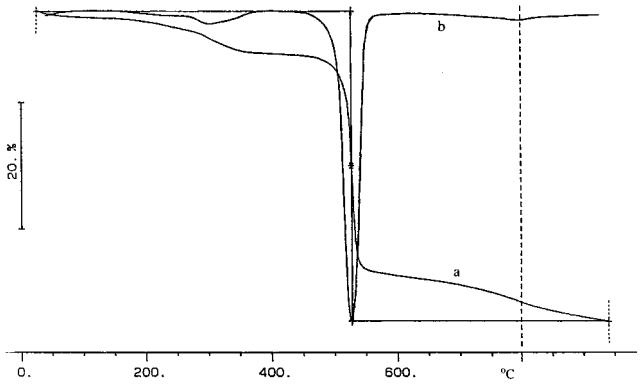


Figure 6. TGA curve of polymer **(−)-5b** from 20 to 800 °C, heating rate 10 °C/min: (a) weight loss in percent; (b) derivative of the weight loss.

of other important materials that exhibit a large thermal stability.[26] It should be taken into account, however, that, as mentioned above, the heating reduces the M_w, indicating a degradation process of the polymeric chains not resulting in weight loss.

In the DSC curves, only for **1b** and **3** could clearly be observed a glass transition at 220 and 167 °C, respectively, with reasonable ΔC_p values (0.11 and 0.23 J g^{-1} K^{-1}). In the case of **4**, an increase of C_p of 0.09 J g^{-1} K^{-1} was apparent at 157 °C, but this is inside the decomposition temperature of the polymer, and in the case of **5**, no step attributable to a glass transition could be detected below 250 °C, suggesting that the T_g might be higher.

The DSC curve of the PTHF-containing ketone polymer **2a** showed an intense endothermic peak near −50 °C that is absent in the case of the **2b**, which is free of PTHF, for which we have not found a suitable explanation. We have already observed[2,4] that the DSC curves of the phosphazene−PTHF blends exhibit the transitions corresponding to the melting and crystallization of the PTHF domains, but at 27 °C (endothermic) and −20 °C (exothermic). In fact, those features are present in the case of **1a**, although absent in **5a**. A more comprehensive study of this problem is currently under way.

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