Preparation of a New Type of Phosphazene High Polymers Containing 2,2′-Dioxybiphenyl Groups

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ABSTRACT: The direct reaction of $[NPCl_2]_n$ with the difunctional reagent 2,2′-dihydroxybiphenyl ($HOC_6H_4C_6H_4OH$) and K_2CO_3 in tetrahydrofuran gave soluble linear phosphazene high polymers instead of the expected cross-linked products. The reaction of $[N_3P_3Cl_6]$ with 1, 2, or 3 equiv of $HOC_6H_4C_6H_4OH$ and K_2CO_3 in acetone gave the known spiro derivatives $[N_3P_3Cl_4(O_2C_{12}H_8)]$, $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$, and $[N_3P_3(O_2C_{12}H_8)_3]$ without formation of bridging products, and the dichloro derivative reacted directly with para-substituted phenols HOC_6H_4R and K_2CO_3 in acetone to give the new compounds $[N_3P_3(OC_6H_4R)_2(O_2C_{12}H_8)_2]$ (R = Br, COC_6H_5, or OCH_3), without signs of replacement of the bis(aryloxy) substituents. In an analogous manner, poly(dichlorophosphazene) $[NPCl_2]_n$ reacted with $HOC_6H_4C_6H_4OH$ and K_2CO_3 in THF without significant cross-linking to give, depending on the mole ratio, the soluble polymer $[NP(O_2C_{12}H_8)]_n$ (M_w = 450 000, T_g = 160 °C) or the partially substituted polymers $\{[NP(O_2C_{12}H_8)]_{0.35}[NPCl_2]_{0.65}\}_n$. The latter were subsequently reacted with the para-substituted phenols HOC_6H_4R and K_2CO_3 in THF to give the random copolymers $\{[NP(O_2C_{12}H_8)]_{0.35}[NP(OC_6H_4R)_2]_{0.65}\}_n$ [R = Br, CN, $COCH_3$, or COC_6H_5). The new polymers are soluble (except the CN derivative, which was sparingly soluble) white solids, with only a few ppm of unreacted chlorine, and M_w of the order of 1 000 000 with polydispersities varying from 3 to 10. The T_g values varied with R ranging from 73 °C (R = CN) to 54 °C (R = COMe).

Introduction

Poly[alkoxy- or -(aryloxy)phosphazenes] of the general formula $[NP(OR)_{2-x}(OR')_x]_n$ (R = R′, homopolymers; R ≠ R′, copolymers) are a very important class of inorganic macromolecules.[1] They are usually prepared by reacting $[NPCl_2]_n$ and the NaOR, NaOR′ salts in an appropriate organic solvent. As a result, many different organic groups can be incorporated to the main chain and in variable proportions leading to multifunctionalized polymers. On the other hand, many of their mechanical and other physical properties, especially solubility and hydrophobicity, markedly depend on their chemical composition. Therefore, the polyphosphazenes can be tailored aiming for different predetermined properties.[2] Furthermore, controlled cross-linking allow the preparation of functionalized elastomers that are useful materials for many different applications.[3]

So far, the only limitation appeared to be the use of difunctional reagents, because of the high probability that their reactions with $[NPCl_2]_n$ lead to cross-linking in the first steps of the chlorine substitution process giving unstable insoluble materials.[3]

Recently, we reported[4] a very convenient method for the preparation of trimeric and polymeric (aryloxy)-phosphazenes directly from $[N_3P_3Cl_6]$ or $[NPCl_2]_n$, phenols, and K_2CO_3 using acetone (for the trimers) or tethahydrofuran (for the polymers) as solvent. While extending the application of the method to the diol 2,2′-dihydroxybiphenyl ($HOC_6H_4C_6H_4OH$), we noted that the reactions with $[N_3P_3Cl_6]$ were very clean, leading to the mono-spiro-, bis-spiro and tris-spiro-substituted derivatives without signs of intramolecular or intermolecular bridged species. This prompted us to try the reaction of poly(dichlorophosphazene) $[NPCl_2]_n$ with this diol and K_2CO_3 in THF which gave soluble polymers of formula $\{[NP(O_2C_{12}H_8)]_{1-x}[NPCl_2]_x\}_n$, including the totally substituted derivative $[NP(O_2C_{12}H_8)]_n$, which was also soluble.

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Experimental Section

Materials. K_2CO_3 was dried at 140 °C prior to use. The acetone used as solvent was predistilled from $KMnO_4$ and further distilled from anhydrous $CaSO_4$. The THF was treated with KOH and distilled twice from Na in the presence of benzophenone. Petroleum ether refers to that fraction with boiling point in the range 60−65 °C. The diphenol $HOC_6H_4C_6H_4OH$ and the phenols HOC_6H_4R (R = Br, CN, $COCH_3$, COC_6H_5, OCH_3) were used as purchased (Aldrich). The hexachlorocyclotriphosphazene $[N_3P_3Cl_6]$ (Strem Chemicals) was purified from hot petroleum ether and dried in vacuo. Tetrabutylammonium bromide (TBAB) (Aldrich) was dried under vacuum at 50 °C. The starting polymer $[NPCl_2]_n$ was prepared as described by Magill et al.[7] All the reactions were carried out under dry nitrogen.

Measurements. The IR spectra were recorded with a Perkin-Elmer FT 1720-X spectrometer. NMR 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 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. P, Cl, and K analyses were performed by Galbraith Laboratories. Unless stated otherwise, the analytical data given for the cyclic phosphazenes correspond to the isolated reaction products without purification. GPC were measured with a Perkin-Elmer instrument with a Model LC 250 pump, a Model LC 290 UV, and a Model LC 30 refractive index detector. The samples were eluted with a 0.1% by weight solution of tetra-*n*-butylammonium bromide in THF through Perkin-Elmer PLGel (Guard 10^5, 10^4, and 10^3 Å) at 30 °C. Approximate molecular weight 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. 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 °C under constant flow of nitrogen.

Synthesis of the Cyclic and Polymeric Phosphazenes. $[N_3P_3Cl_4(O_2C_{12}H_8)]$ (1). A mixture of $[N_3P_3Cl_6]$ (0.5 g, 1.44

mmol), 2,2′-$HOC_6H_4C_6H_4OH$ (0.268 g, 1.44 mmol), and K_2CO_3 (1 g, 7.24 mmol) in acetone (20 mL) was stirred at room temperature for 15 min. The volatiles were evaporated in vacuo, and the residue was extracted with CH_2Cl_2 (3 × 15 mL). Evaporation of the solvent in vacuo gave **1** as a white solid, containing ca. 3% of **2**, yield 0.6 g, 91%. Recrystallization from CH_2Cl_2/petroleum ether gave the pure product.

^{1}H NMR δ: 7.2−7.6 (m, 8 H, $C_{12}H_8$). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 13.3 (dd, 1P, $P(O_2C_{12}H_8)$), 25.2 (d, 2P, PCl_2) (AB_2 system, J_{AB} = 71); (acetone/D_2O) 14.0 (dd, 1P, $P(O_2C_{12}H_8)$), 25.8 (d, 2P, PCl_2) (AB_2 system, J_{AB} = 72). $^{13}C\{^1H\}$ NMR 122 (d, J_{PC} = 4), 128 s, 129 s, 130.6 s, 130.9 s, 148 m (12 C; $C_{12}H_8$). Anal. Calcd for $C_{12}H_8O_2Cl_4N_3P_3$: C, 31.3; H, 1.7; N, 9.1. Found: C, 31.7; H, 1.8; N, 8.9.

$[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ (2). To a solution of 2,2′-$HOC_6H_4C_6H_4$-OH (0.53 g, 2.88 mmol) in acetone (15 mL), which was cooled to 0 °C, were added solid $[N_3P_3Cl_6]$ (0.5 g, 1.44 mmol) and K_2CO_3 (1 g, 7.23 mmol) and the mixture was stirred at room temperature for 2 h. The volatiles were evaporated in vacuo and the residue extracted with CH_2Cl_2 (5 × 25 mL). Evaporation of the solvent in vacuo gave **2** as a white solid, containing 1−3% of **3**, yield 0.69 g, 83%.

^{1}H NMR δ: 7.3−7.5 (m, 16H, $C_{12}H_8$). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 19.9 [d, 2P, $P(O_2C_{12}H_8)$], 29.6 (dd, 1P, PCl_2) (AB_2 system, J_{AB} = 80); (acetone/D_2O) 20.7 [d, 2P, $P(O_2C_{12}H_8)$], 29.8 (dd, 1P, PCl_2) (AB_2 system, J_{AB} = 81). $^{13}C\{^1H\}$ NMR 122 s, 127 s, 129 s, 130.5 s, 130.7 s, 148 m (24 C; $C_{12}H_8$). Anal. Calcd for $C_{24}H_{16}O_4Cl_2N_3P_3$: C, 50.2; H, 2.8; N, 7.3. Found: C, 49.7; H, 2.7; N, 7.0.

$[N_3P_3(O_2C_{12}H_8)_3]$ (3). A mixture of $[N_3P_3Cl_6]$ (0.5 g, 1.44 mmol), 2,2′-$HOC_6H_4C_6H_4OH$ (0.9 g, 4.83 mmol), and K_2CO_3 (1.5 g, 10.9 mmol) in acetone (70 mL) was refluxed for 5 h. The volatiles were evaporated in vacuo, and the residue was washed with water (50 mL), aqueous NaOH (50 mL, 0.5 M), water (2 × 50 mL), ethanol (25 mL), and ether (25 mL). The product was dried in vacuo, yield 0.85 g, 86%. The products, not further purified, had a moderate analytical purity with lower than expected C,H,N values.

^{1}H NMR δ: 7.2−7.6 (m, 24 H, $C_{12}H_8$). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 26; (acetone/D_2O) 27 (s, 3 P, N_3P_3 ring). Anal. Calcd for $C_{36}H_{24}O_6N_3P_3$: C, 62.9; H, 3.5; N, 6.1. Found: C, 61.1; H, 3.4; N, 5.8.

$[N_3P_3(OC_6H_4\text{-}Br)_2(O_2C_{12}H_8)_2]$ (4a). A mixture of $[N_3P_3Cl_2$-$(O_2C_{12}H_8)_2]$ (0.8 g, 1.39 mmol), HOC_6H_4Br (0.481 g, 2.78 mmol), and K_2CO_3 (2 g, 14.5) in acetone (40 mL) was refluxed for 3 h. The volatiles were evaporated in vacuo and the residue extracted with CH_2Cl_2 (4 × 15 mL). Evaporation of the solvent in vacuo gave pure **4a** as a white solid, yield 1.1 g, 95%.

^{1}H NMR δ: 7.0−7.5 (m 24 H, arom rings). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 10.3 (dd, 1P, $P(OC_6H_4Br)_2$) 25.7 (d, 2P, $P(O_2C_{12}H_8)$) (AB_2 system, J_{AB} = 93); (acetone/D_2O) 11.6 (dd, 1P, $P(OC_6H_4$-$Br)_2$), 26.7 (d, 2P, $P(O_2C_{12}H_8)$) (AB_2 system, J_{AB} = 93). $^{13}C\{^1H\}$ NMR: 119, 122, 124 (d, J_{PC} = 5 Hz), 127, 129, 130.3, 130.4, 133 s, 149 br, 150 br (36 C; arom rings). Anal. Calcd for $C_{36}H_{24}O_6Br_2N_3P_3$: C, 51.0; H, 2.9; N, 5.0. Found: C, 50.8; H, 2.9; N, 4.5.

$[N_3P_3(OC_6H_4\text{-}COC_6H_5)_2(O_2C_{12}H_8)_2]$ (4b). A mixture of $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ (0.5 g, 0.83 mmol), $HOC_6H_4COC_6H_5$ (0.34 g, 1.74 mmol), and K_2CO_3 (0.6 g, 4.35 mmol) in acetone (30 mL) was refluxed for 1 h. The volatiles were evaporated in vacuo, and the residue was extracted with CH_2Cl_2 (4 × 40 mL). The solution was evaporated in vacuo to give pure **4b** as a white solid, yield 0.65 g, 88%.

^{1}H NMR δ: 7.0−8.0 (m, 34 H, arom rings). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 9.5 (dd, 1P, $P(OC_6H_4COC_6H_5)_2$), 25.6 (d, 2P, $P(O_2C_{12}H_8)$) (AB_2 system, J_{AB} = 95); (acetone/D_2O) 11.2 (dd, 1P, $P(OC_6H_4$-$COC_6H_5)_2$), 26.7 (d, 2P, $P(O_2C_{12}H_8)$) (AB_2 system, J_{AB} = 95 Hz). $^{13}C\{^1H\}$ NMR: 122.3, 127, 129, 130.3, 130.4, 130.6, 132.6, 133, 135, 138, 149, 154 (48 C, arom rings), 196 (2C, CO). Anal. Calcd for $C_{50}H_{34}O_8N_3P_3$: C, 66.9; H, 3.8; N, 4.7. Found: C, 65.8; H, 4.0; N, 4.5.

Synthesis of $[N_3P_3(OC_6H_4OCH_3)_2(O_2C_{12}H_8)_2]$ (4c). A mixture of $[N_3P_3Cl_2(O_2C_{12}H_8)_2]$ (1 g, 1.74 mmol), HOC_6H_4OMe (0.431 g, 3.47 mmol), TBAB (0.04 g, 0.12 mmol), and K_2CO_3 (2 g, 14.5 mmol) in acetone (35 mL) was refluxed for 6.5 h. The volatiles were evaporated in vacuo, and the residue was dissolved in toluene (100 mL). The solution was washed with water (3 × 200 mL). The solvent was evaporated, the residue was dissolved in CH_2Cl_2, and the solution was dried over Na_2SO_4. After filtering, the solvent was evaporated in vacuo to give pure **4c** as a white solid, yield 1.12 g, 86.3%.

^{1}H NMR δ: 3.7 (s, 6H, OCH_3), 6.8−7.4 (m, 24 H, arom rings). $^{31}P\{^1H\}$ NMR: ($CDCl_3$) 11.1 (dd, 1P, $P(OC_6H_4OMe)_2$), 26.2 (d, 2P, $P(O_2C_{12}H_8)$) (AB_2 system, J_{AB} = 91); (acetone/D_2O) 12.4 (dd, 1P, $P(OC_6H_4OMe)_2$), 27 (d, 2P, $P(O_2C_{12}H_8)$) (AB_2 system, J_{AB} = 92). $^{13}C\{^1H\}$ NMR: 56.3 (s, 2C, OCH_3), 115, 122.5, 122.8 (d, J_{PC} = 4), 127, 129, 130.2, 130.3, 145 br, 149 br, 157 (36 C, arom rings). Anal. Calcd for $C_{38}H_{30}O_8N_3P_3$: C, 60.9; H, 4.0; N, 5.6. Found: C, 60.7; H, 4.3; N, 5.2.

$[NP(O_2C_{12}H_8)\cdot x(OC_4H_8)]_n$ (5). To a solution of $[NPCl_2]_n$ (1.85 g, 16 mmol) in THF (300 mL) were added 2,2′-$HOC_6H_4C_6H_4OH$ (4.5 g, 24 mmol) and K_2CO_3 (8.8 g, 63.8 mmol), and the mixture was refluxed for 35 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 into water (1.5 L). The product was similarly reprecipitated once from THF/2-propanol and once from THF/petroleum ether. The resulting solid was predried first in vacuo at room temperature and then at 70 °C for 7 days. The product was $[NP(O_2C_{12}H_8)\cdot 0.4(OC_4H_8)]_n$ (11.2% poly-THF), yield 2.3 g, 56%.

^{1}H NMR δ: 6.6−7.4 (m, 8 H, arom rings), 3.4m, 1.6m (3.2 H, poly-THF). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −5.82 (−6.06 in THF). $^{13}C\{^1H\}$ NMR: 124, 126, 129, 130, 149 ($C_{12}H_8O_2$), 27.2, 71.3 (poly-THF). Anal. Calcd for $C_{13.6}H_{11.2}O_{2.4}NP$: C, 63.3; H, 4.3; N, 5.4; P, 12.0. Found: C, 63.4; H, 4.1; N, 5.4; P, 12.3. Chlorine content 0.16%.

M_w(GPC) 385 000 (M_w/M_n = 5.5). T_g(DSC) = 164 °C.

TGA: −11.5% (360 °C), −46% (480 °C). Residue at 800 °C: 37%.

A similar preparation but with a reaction time of 23 h gave the product $[NP(O_2C_{12}H_8)\cdot 0.5(OC_4H_8)]_n$ (13.8% poly-THF) in 60% yield. Anal. Calcd for $C_{14}H_{12}O_{2.5}NP$: C, 63.4; H, 4.5; N, 5.3; P, 11.7. Found: C, 64.4; H, 4.3; N, 5.4; P, 11.7. Chlorine content: 0.085%. K content: 0.0082%.

M_w(GPC) 620.000 (M_w/M_n = 8.0). T_g(DSC) = 160 °C.

TGA: −14.3% (350 °C); −46.5% (480 °C). Residue at 800 °C: 34%.

Using an excess of 6 mmol of 2,2′-$HOC_6H_4C_6H_4OH$ per mmol of $[NPCl_2]_n$ and 35 h of reflux gave the product $[NP(O_2C_{12}H_8)]_n$ free of poly-THF in 59% yield. Anal. Calcd for $C_{12}H_8O_2NP$: C, 62.9; H, 3.5; N, 6.1; Found: C, 62.6; H, 3.5; N, 6.0.

M_w(GPC) 490 000 (M_w/M_n = 9.9). T_g(DSC) = 160 °C.

TGA: −63% (470 °C). Residue at 800 °C: 28%.

$\{[NP(O_2C_{12}H_8)]_{0.35}[NP(OC_6H_4Br)_2]_{0.65}\cdot x(OC_4H_8)\}_n$ (6a). To a solution of $[NPCl_2]_n$ (1.43 g, 12.3 mmol) in THF (250 mL) were added 2,2′-$HOC_6H_4C_6H_4OH$ (0.76 g, 4.1 mmol) and K_2CO_3 (6.82 g, 49.2 mmol), and the mixture was refluxed for 1.5 h with vigorous mechanical stirring. Then, the phenol HOC_6H_4-Br (14.2 g, 82.2 mmol) was added, and refluxing was continued for 72 h. After that, the polymer **6a** was isolated and purified following the same procedure as for **5**. Yield: 2.5 g, 60%. The product had x = 0.08 (1.7% poly-THF).

^{1}H NMR δ: 6.4−7.5 (m, arom rings). $^{31}P\{^1H\}$ NMR ($CDCl_3$): −4.3 [m, $P(O_2C_{12}H_8)$], −20.3 [m, $P(OC_6H_4Br)_2$], (−4.0 and −20.0 in THF). $^{13}C\{^1H\}$ NMR: 118, 123, 133, 151 (OC_6H_4-Br), 123(sh), 126, 129.5, 130, 149 ($C_{12}H_8O_2$). Anal. Calcd for $C_{12.3}H_{8.6}O_{2.08}NPBr_{1.3}$: C, 43.6; H, 2.5; N, 4.1; P, 9.2. Found: C, 43.9; H, 2.5; N, 4.2; P, 9.4.

M_w(GPC) 1 400 000 (M_w/M_n = 8.1). T_g(DSC) = 55 °C.

TGA: −1.6% (320 °C), −55% (480 °C). Residue at 800 °C: 41%.

The same results were obtained using a ratio of 2.7 mmol of bromophenol and 200 h reflux in the second substitution step.

In another experiment the $[NPCl_2]_n$ was reacted first for 16 h with 0.53 mmol of 2,2′-$HOC_6H_4C_6H_4OH$ and then for 67 h with 2.4 mmol of bromophenol per mmol of still unreacted $(NPCl_2)$ to give the polymer $\{[NP(O_2C_{12}H_8)]_{0.55}[NP(OC_6H_4$-$Br)_2]_{0.45}\cdot 0.1(OC_4H_8)\}_n$ (2.33% poly-THF), isolated in 58% yield. Anal. Calcd for $C_{12.4}H_{8.8}O_{2.1}NPBr_{0.9}$: C, 48.3; H, 2.8; N, 4.5.

Found: C, 47.6; H, 2.8; N, 4.4; $M_w = 1\ 290\ 000$ ($M_w/M_n = 5.2$). T_g(DSC) = 72 °C.

TGA: −2.8% (340 °C), −51.9%(480 °C). Residue at 800 °C: 44%.

{[NP(O$_2$C$_{12}$H$_8$)]$_{0.35}$[NP(OC$_6$H$_4$CN)$_2$]$_{0.65}$}$_n$ (6b). To a solution of [NPCl$_2$] (1.43 g, 12.3 mmol) in THF (250 mL) were added 2,2′-HOC$_6$H$_4$C$_6$H$_4$OH (0.76 g, 4.12 mmol) and K$_2$CO$_3$ (6.8 g, 49.2 mmol), and the mixture was refluxed for 1.5 h with vigorous mechanical stirring. Then, the phenol HOC$_6$H$_4$CN (2.94 g, 24.7 mmol) was added, and refluxing was continued for 65 h. The mixture was poured into water (1.5 L) to give a white precipitate that was dissolved in DMF. The solution was filtered and concentrated to a viscous liquid that was poured into water (1.5 L). The precipitate was washed with 2-propanol and hexane. The resulting solid was predried first in vacuo at room temperature and then at 70 °C for 7 days, yield 2.3 g, 71%. When freshly precipitated from DMF/H$_2$O the polymer is soluble in THF.

^{31}P{^{1}H} NMR (DMF): −3.3 [m, P(O$_2$C$_{12}$H$_8$)], −20.8 [m, P(OC$_6$H$_4$CN)$_2$]. Anal. Calcd for C$_{13.3}$H$_8$O$_2$N$_{2.3}$P: C, 60.7; H, 3.0; N, 12.2; P, 11.8. Found: C, 60.0; H, 2.9; N, 11.9; P, 12.1. Chlorine content 0.04%.

$M_w = 1\ 680\ 000$ ($M_w/M_n = 2.1$). T_g(DSC) = 75 °C.

TGA: continuous loss of weight more pronounced at ca. 320 and 440 °C. Residue at 800 °C: 45%.

{[NP(O$_2$C$_{12}$H$_8$)]$_{0.35}$[NP(OC$_6$H$_4$COCH$_3$)$_2$]$_{0.65}$}$_n$ (6c). To a solution of [NPCl$_2$]$_n$ (1.26g, 10.9 mmol) in THF (240 mL) were added 2,2′-HOC$_6$H$_4$C$_6$H$_4$OH (0.67 g, 3.62 mmol) and K$_2$CO$_3$ (6.01 g, 43.5 mmol), and the mixture was refluxed for 1 h with vigorous mechanical stirring. Then, the phenol HOC$_6$H$_4$COCH$_3$ (2.97 g, 21.8 mmol) was added, and refluxing was continued for 62 h. After that, the polymer **6c** was isolated and purified following the same procedure as for **5**, yield 2.3 g, 74%.

^{1}H NMR δ: 2.2 (CH$_3$), 6.4−7.5 (m, arom rings). ^{31}P{^{1}H} NMR (CDCl$_3$): −4.2 [m, P(O$_2$C$_{12}$H$_8$)], −20.8 [m, P(OC$_6$H$_4$COCH$_3$)$_2$] (−3.9 and −20.2 in THF). ^{13}C{^{1}H} NMR: 27 (2C, CH$_3$), 197 (2C, CO), 121, 130, 134, 155 (C$_6$H$_4$), 122, 126, 129, 149 (C$_{12}$H$_8$O$_2$). Anal. Calcd for C$_{14.6}$H$_{11.9}$O$_{3.3}$NP: C, 61.5; H, 4.2; N, 4.9; P, 10.9. Found: C, 61.0; H, 4.1; N, 4.9; P, 11.0. Chlorine content 0.1%.

M_w(GPC) 1 650 000 ($M_w/M_n = 3.7$). T_g(DSC) = 54 °C.

TGA: continuous loss of weight more pronounced at 310, 520 °C. Residue at 800 °C: 65%.

{[NP(O$_2$C$_{12}$H$_8$)]$_{0.35}$[NP(OC$_6$H$_4$COC$_6$H$_5$)$_2$]$_{0.65}$}$_n$ (6d). To a solution of [NPCl$_2$]$_n$ (2.1 g, 18.6 mmol) in THF (300 mL) were added 2,2′-HOC$_6$H$_4$C$_6$H$_4$OH (1.1 g, 6.2 mmol) and K$_2$CO$_3$ (10.3 g, 74.2 mmol), and the mixture was refluxed for 1 h with vigorous mechanical stirring. Then, the phenol HOC$_6$H$_4$COC$_6$H$_5$ (7.2 g, 36.32 mmol) was added, and refluxing was continued for 62 h. After that, the polymer **6d** was isolated and purified following the same procedure as for **5**, yield 5.1 g, 75%.

^{1}H NMR δ: 6.4−7.5 (m, arom rings). ^{31}P{^{1}H} NMR (CDCl$_3$): −4.1 [m, P(O$_2$C$_{12}$H$_8$)], −21.5 [m, P(OC$_6$H$_4$COC$_6$H$_5$)$_2$] (−4.2 and −21.1 in THF). ^{13}C{^{1}H} NMR: 195 (2C, CO), 121, 129, 130, 132, 133, 134, 138, 155 (C$_6$H$_5$ and C$_6$H$_4$), 122, 126, 129, 130, 149 (C$_{12}$H$_8$O$_2$). Anal. Calcd for C$_{21.1}$H$_{14.5}$O$_{3.3}$NP: C, 69.3; H, 4.0; N, 3.8; P, 8.4. Found: C, 69.6; H, 4.1; N, 3.7; P, 8.3. Chlorine content 0.06%.

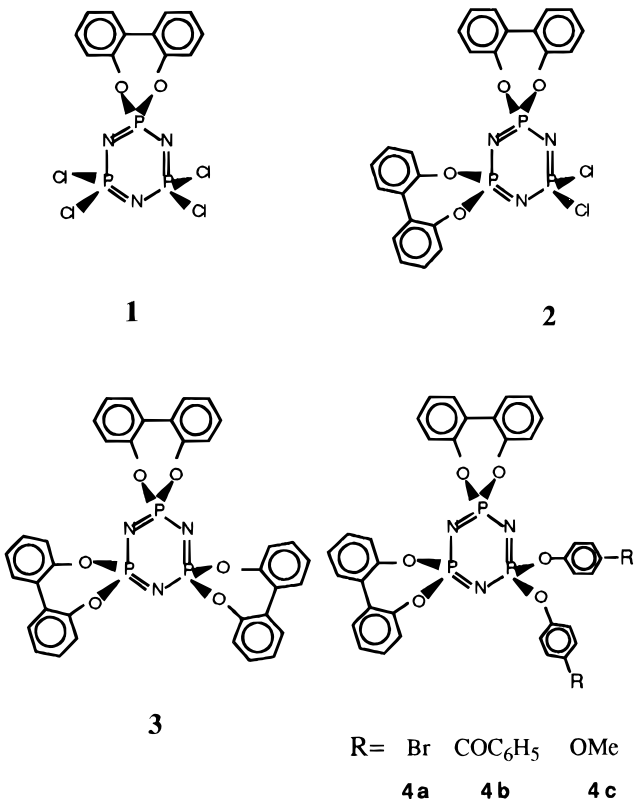
M_w(GPC) 1 250 000 ($M_w/M_n = 3.1$). T_g(DSC) = 68 °C.

TGA: continuous loss of weight more pronounced at 450 °C. Residue at 800 °C: 50%.

Results and Discussion

The hexachlorocyclotriphosphazene [N$_3$P$_3$Cl$_6$] reacted with the diol 2,2′-HOC$_6$H$_4$C$_6$H$_4$OH in the presence of K$_2$CO$_3$ in acetone to give, depending on the conditions, the known[5] substituted products [N$_3$P$_3$Cl$_4$(O$_2$C$_{12}$H$_8$)] (**1**), [N$_3$P$_3$Cl$_2$(O$_2$C$_{12}$H$_8$)$_2$] (**2**), and [N$_3$P$_3$(O$_2$C$_{12}$H$_8$)$_3$] (**3**) (Chart 1). At room temperature, with a 1:1 ratio, the reaction gave **1** with ca. 3% of **2** and, with a 1:2 ratio, compound **2** with 1−3% of the tris-spiro derivative **3**. The latter, which is only sparingly soluble, was formed with a 1:3 ratio at reflux. Consistent with earlier observations,[4] the formation of **3** from the diol is faster in acetone than in THF.

Chart 1



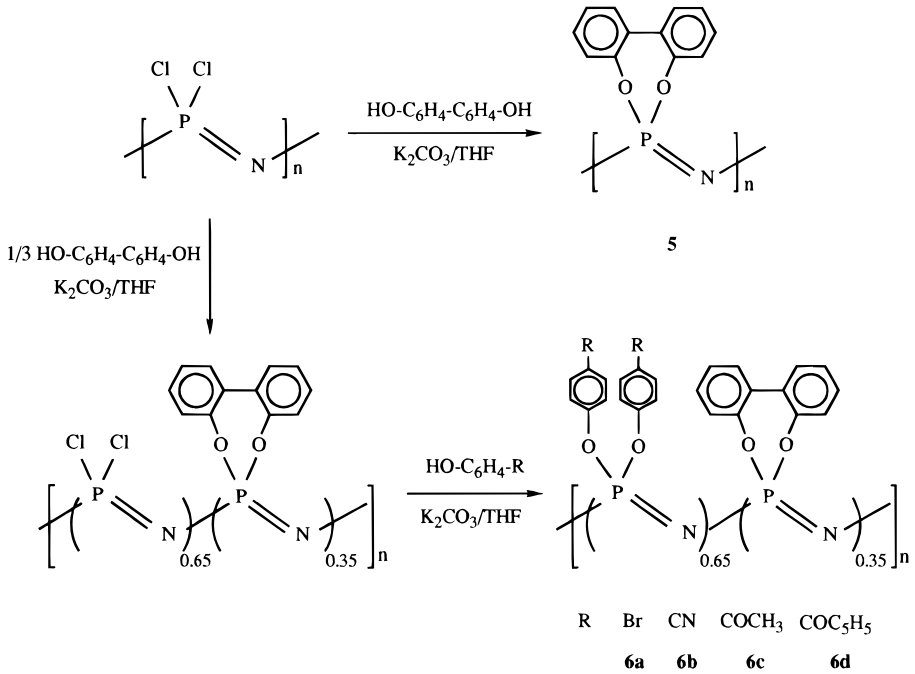
The dichloro derivative **2** reacted very fast with para-substituted phenols HOC$_6$H$_4$R and K$_2$CO$_3$ in refluxing acetone to give [N$_3$P$_3$(OC$_6$H$_4$R)$_2$(O$_2$C$_{12}$H$_8$)$_2$] R = Br (**4a**) and COC$_6$H$_5$ **(4b)** that were isolated pure in high yield. However, with the less acidic phenol HOC$_6$H$_4$OMe, the reaction was slow and was better carried out in the presence of a small amount of TBAB to give pure [N$_3$P$_3$(OC$_6$H$_4$OMe)$_2$(O$_2$C$_{12}$H$_8$)$_2$] (**4c**).

In no case was the replacement of the O$_2$C$_{12}$H$_8$ groups already present in the cyclic compounds by the entering OC$_6$H$_4$R groups detected.

All the products were characterized by C,H,N analyses, ^{31}P NMR, ^{1}H and ^{13}C NMR (Experimental Section), and mass spectral data. The mass spectra showed the parent peak and the peaks of the fragments left after the sequential loss of OR groups. However, in many cases the fragmentations of the bonds of the *O*-aryl ring and the C$_6$H$_4$−R bonds or bonds inside the R substituent were clearly observed.

It is known that bifunctional nucleophiles can react with [N$_3$P$_3$Cl$_6$] in various ways[6] and that 2,2′-dihydroxybiphenyl HOC$_6$H$_4$C$_6$H$_4$OH can behave as a monofunctional phenol or give transannular substituted cyclic phosphazenes.[5c] However, the observation that its reaction with [N$_3$P$_3$Cl$_6$] and K$_2$CO$_3$ gave no products having intermolecular (bino) or intramolecular (ansa) bridging dioxybiphenyl prompted us to investigate the reactions of this diphenol with the polymer [NPCl$_2$]$_n$ (see Scheme 1). Thus, we found that the poly(dichlorophosphazene), prepared by the thermal polymerization of [N$_3$P$_3$Cl$_6$] in solution,[7] reacted in refluxing THF with 2,2′-dihydroxybiphenyl HOC$_6$H$_4$C$_6$H$_4$OH in the presence of K$_2$CO$_3$ to give after 35 h the new polymer [NP(O$_2$C$_{12}$H$_8$)]$_n$ (**5**) in ca. 60% yield. The isolated products

Scheme 1



were very soluble in THF and CH_2Cl_2 and had less than 0.1% of chlorine (when the reaction time was reduced to 12 h the polymer contained 0.6% of unreacted Cl) and no traces of K-salts (less than 0.009% K). Therefore, no significant cross-linking took place during the substitution reaction. The average M_w, as measured by GPC, was of the order of 500 000 with a polydispersity of 5−10. Rather unexpectedly, however, the chromatograms indicated that the products were reproducibly bimodal (Figure 1).

All the analytical and spectroscopic data (Experimental Section) were in accord with the formulation of **5** (Scheme 1) and clearly evidenced the complete (or at least nearly so) spiro ring formation in the high polymers. Thus, the ^{13}C NMR spectra showed only five peaks (one of them, at 130 ppm, corresponding to two carbons) for the $O_2C_{12}H_8$ group (as in the cyclic models), suggesting that it is symmetrycally attached to the P atom. Furthermore, the IR spectra of the solids did not show any indication of free −OH groups, and, moreover, the ^{31}P NMR spectra of both the homopolymers $[NP(O_2C_{12}H_8)]_n$ and the nonisolated precursors $\{[NPCl_2]_x[NP(O_2C_{12}H_8)]_{1-x}\}_n$ clearly show that there were no signals attributable to groups $[NP(OC_{12}H_8OH)_2]$ with monodentated biphenols (that, according to the spectra of the copolymers $\{[NP(OC_6H_4R)_2]_x$-$[NP(O_2C_{12}H_8)]_{1-x}\}_n$ (**6** in Scheme 1, as described below) would have ^{31}P chemical shifts of the order of −20 ppm).

However, in all the preparations performed (except in one, which was carried out using a large excess of diol) the final products contained variable ammounts of poly(tetrahydrofuran) (poly-THF) and had the composition $[NP(O_2C_{12}H_8)\cdot x(OC_4H_8)]_n$, with x ranging from 0.1 to 0.5. This was supported by the analytical data and by the ^1H NMR spectra (two equally intense signals at 1.6 and 3.4 ppm, with the exact integration required for each x value), and the ^{13}C NMR spectra (two signals at 27.1 and 71.3 ppm) (for the cyclic THF the signals are at 1.8 and 3.7 and at 26.7 and 68.6 ppm, respectively). The poly-THF contents were unaltered after the polymers were dried at 70 °C for 30 days, and repeated reprecipitations from CH_2Cl_2/petroleum ether caused only slight reductions. Significant elimination of poly-THF (e.g., from $x = 0.4-0.2$) occurred on heating the polymers at 190 °C for 4 h. This treatment provoked the depolymerization and volatilization of the poly-THF but also reduced the average molecular weight of the product to ca. 300 000 ($M_w/M_n = 6.0$) and the T_g to 158 °C, indicating that the heating also caused the fragmentation of the phosphazene chains. Thus, a 24 h drying at this temperature almost eliminated the poly-THF content, giving an average M_w of 290 000 ($M_w/M_n = 4.7$) (T_g of 141 °C) (in both cases the bimodality was the same than that of the starting material). Consistently, the TGA curves of the products showed a weight loss at 360 °C that matched their poly-THF contents.

The DSC curves of **5** exhibited a very clear glass transition with T_g around 161 °C and gave further confirmation of the poly-THF content because they showed an endothermic peak in the heating curves at 27 °C and an exothermic one in the cooling processes at −20 °C that were absent in the samples without poly-THF. This transition fits well with the expected value[8] for the melting point (and freezing point) of poly-THF of average molecular weights intermediate between 2000 and 3000.

After a number of experiments, it was concluded that the poly-THF was formed when the $[NPCl_2]_n$, obtained heating the cyclic $[N_3P_3Cl_6]$ by the method of Magill,[7] was dissolved in THF for its reaction with 2,2′-$HOC_6H_4C_6H_4OH$. This unexpected effect is due to small amounts of sulfamic acid that is used as a promoter of the polymerization of $[N_3P_3Cl_6]$ and that may be occasionally present in the polydichlorophosphazene used in the synthesis of **5**. We checked that, as expected,[9] the sulfamic acid did, in fact, polymerize the THF.

However, the difficulty in eliminating the poly-THF from the isolated polyphosphazenes by repeated precipitations in water, alcohol, and hexane is more puzzling because it is appreciably soluble in those solvents. In fact, no poly-THF contents were reported in the purified polymers prepared by Magill et al.[7] In the same way, the phosphazene polymers prepared earlier by us using the same polymerization method[4] did not

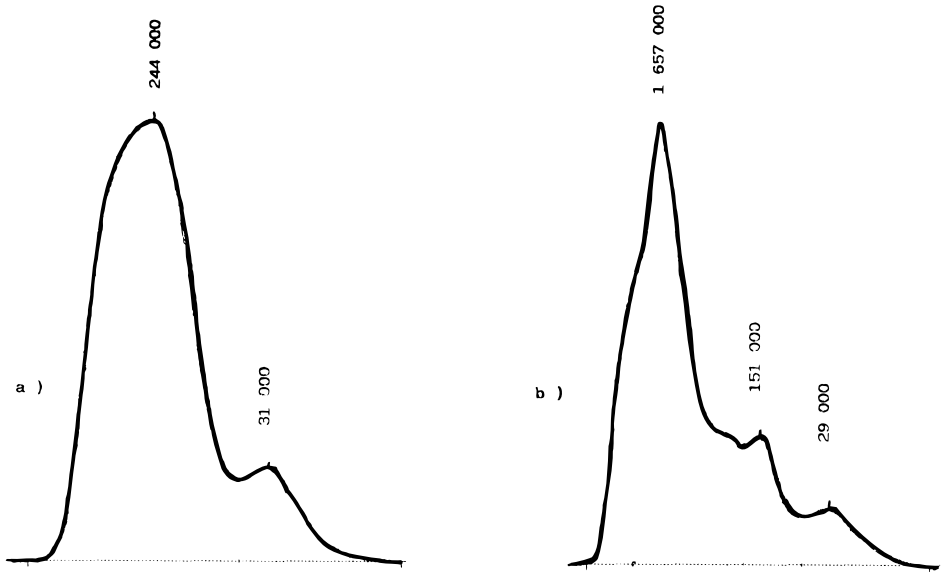


Figure 1. GPC chromatogramms of the polymers **5** (a) and **6a** (b).

contain significant amounts of poly-THF (although we detected very tiny amounts in some of the samples). Thus, it could be argued that, in the case of the polymers **5**, the poly-THF chains could be trapped with the phosphazene chains by entanglements suggesting a strong association favored by the presence of the $P(O_2C_{12}H_8)$ rings. However, although it is known that the cyclic models with some dioxyarenyl groups can form solid structures with channels capable of retaining small molecules,[10] the 2,2′-dioxybiphenyl derivatives do not have this propensity.[11]

The reaction of $[NPCl_2]_n$ with 0.33 mmol of $HOC_6H_4C_6H_4OH$ in the presence of K_2CO_3 gave in 1.5 h the partially substituted polymers with average composition $\{[NP(O_2C_{12}H_8)]_{0.35}[NPCl_2]_{0.65}\}_n$. The latter were subsequently reacted with the acidic phenols HOC_6H_4R and K_2CO_3 in refluxing THF to give the phosphazene random copolymers $\{[NP(O_2C_{12}H_8)]_{0.35}$-$[NP(OC_6H_4R)_2]_{0.65}\}_n$ (**6**) [R = Br, CN, $COCH_3$, or COC_6H_5] that were isolated in 60−70% yields and with a high analytical purity. Monitoring the reaction by ^{31}P NMR clearly indicated that the substitution mechanisms were predominantly nongeminal and that, as in the cyclic models, no appreciable substitution of the $O_2C_{12}H_8$ groups by the entering OC_6H_4R was observed. The reaction time was short (60 h) except for R = Br, which was on the order of 200 h unless a large excess of *p*-bromophenol is used in the second step. The relative proportions of the units $[NP(O_2C_{12}H_8)]$ and $[NP$-$(OC_6H_4R)_2]$ could be easily controlled by varying the amounts of diol and phenol used. Thus, with 0.53 mmol of diol and an excess of HOC_6H_5Br, the polymer $\{[NP(O_2C_{12}H_8)]_{0.55}[NP(OC_6H_4Br)_2]_{0.45}\cdot 0.1(OC_4H_8)\}_n$ was obtained in 58% yield.

The new polymers (having only a few ppm of chlorine) were white solids that, with the exception of the derivative with R = CN, were very soluble in THF and CH_2Cl_2 (the R = CN polymer could be dissolved in DMF). The actual ratios $[NP(O_2C_{12}H_8)]/[NP(OC_6H_4R)_2]$ as measured by integrating the corresponding signals in the ^{31}P NMR were in good agreement within experimental error with the expected 0.35/0.65. The M_w (GPC) were of the order of 1 000 000 with polydispersities varying from 2 to 8 depending on R.

Similar to **5**, some of the products contained ca. 0.1 OC_4H_8 units of poly-THF per $[NP(O_2C_{12}H_8)]_{0.35}[NP$-$(OC_6H_4R)_2]_{0.65}$ unit (representing 1−3% in weight). However, the derivatives with CN, $COCH_3$, and COC_6H_5 were obtained totally pure, free of poly-THT. (In the case of the rather insoluble CN derivative, the poly-THF, which may be occasionally present in some samples, is better detected by the peak at 27 °C in the DSC curves).

The other unexpected feature of the polymers was their bimodal character with reproducible chromatograms (Figure 1), which was almost absent in the case of the derivative with R = COC_6H_5, but very noticeable for **5** and for the mixed derivatives with R = COMe and Br. A plausible explanation could be the fragmentation of the polymeric chains during the reaction of the $[NPCl_2]_n$ with the diphenol, as suggested by the average molecular weight of the homopolymer **5**, which is markedly lower than those of the copolymers.

Apart from the poly-THF loss at 360 °C, the TGA curves showed other losses (see Experimental Section), especially one at near 460 °C that ranged from 35 to 50% depending on R. Similar to other polyphosphazenes, this may be due to the formation of volatile cyclic oligomers by depolimerization.[12] The solid residue at 800 °C varied from 35 to 65% depending on R.

The DSC curves displayed only the heat capacity jump corresponding to the glass transition that depended on R in the expected manner.[2,3] Thus, the highest value (161°C) corresponded to the homopolymer $[NP(O_2C_{12}H_8)]_n$, which was not affected by the poly-THF content. For the random copolymers with OC_6H_4R substituents in the ratio 0.35/0.65 the T_g decreased in the order CN > COC_6H_5 > Br ≈ $COCH_3$. Consistently, the copolymer with OC_6H_5Br in a ca 0.5/0.5 ratio had a higher T_g (72 °C) than **6a**.

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